

# Local-Scaling Transformation Version of Density Functional Theory: Application to Atoms and Diatomic Molecules

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**ABSTRACT:** Applications of the local-scaling transformation version of density functional theory, LS-DFT, to atoms and diatomic molecules are presented. In the case of atoms, explicit kinetic- and exchange-energy functionals for first- and second-row atoms at the Hartree–Fock level are constructed. The emphasis given in LS-DFT to the symmetry problem, namely, to the inclusion of spin and angular momentum restrictions in energy density functionals, is illustrated by the construction of explicit energy functionals (at the Hartree–Fock level) for the  $^1S$ ,  $^3P$  and  $^1D$  terms of the  $1s^22s^22p^2$  configuration of the carbon atom. Also, applications of LS-DFT that go beyond the Hartree–Fock method are presented. In this respect, the decomposition of the electron correlation energy into its dynamical and nondynamical parts is analyzed for the case of four-electron atoms and ions. It is shown that a “reference wave function”—differing from the exact one only in the dynamical correlation energy component—can always be found. Based on this wave function, the correlation energy is partitioned into “long-range” and “short-range” contributions. A method based on a cluster-expansion technique is advanced for the purpose of treating the dynamical “short-range” correlation component. In the case of diatomic molecules, the derivation of coupled first-order integral equations for density transformations of prolate-spheroidal coordinates is discussed. Applications of these density transformations to molecular orbitals involving single  $\zeta$  atomic functions are

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carried out and a comparison is made between the energies coming from the original and the locally scaled orbitals. Also, the minimization of the kinetic energy at fixed Hartree–Fock density is discussed as this procedure is equivalent to solving the Kohn–Sham *x-only* equations. Finally, some extensions of LS-DFT to polyatomic systems (molecules and solids) are discussed. In particular, the possibility of generating a molecular energy functional as a collection of atom-centered functionals and of applying nonisotropic density transformations to solids is considered. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 155–183, 1999

## Introduction

The local-scaling transformation version of density functional theory, LS-DFT<sup>1–3</sup> is a constructive approach to DFT that employs, as basic ingredients, density-dependent coordinates. The latter are obtained by means of a generalized coordinate scaling involving an initial and a final density. If the former is known, then the transformation depends on the final density, which may therefore be treated as the unknown variable (for details, see Appendixes A and B).

The way in which these density-dependent coordinates relate to the problem of calculating the energy of a many-electron system is as follows. Given an initial many-electron wave function and then applying local-scaling transformations to each one of the coordinates describing the electron positions we can generate a transformed wave function that is density-dependent both through its transformed coordinates as well as through the Jacobian of the coordinate transformation. By evaluating the expectation value of this transformed wave function with respect to the many-particle Hamiltonian, we obtain, *by construction*, a density-dependent functional. If in this functional we treat the final density as the variational variable, we can minimize the energy by evaluating this functional over all permissible functions representing the final density.

The ideas on which LS-DFT is based are not entirely new. In fact, density-dependent coordinate transformations had already appeared in the works of Macke in 1955,<sup>4</sup> of March and Young in 1958,<sup>5</sup> and of Hall in 1960<sup>6</sup> (among others<sup>7–9</sup>) and the construction of general energy-density functionals involving these transformations was independently advanced in 1983 by Nyden and Parr,<sup>10</sup> Ludeña,<sup>11</sup> Zumbach and Maschke,<sup>12</sup> and further extended later by Ghosh and Parr,<sup>13</sup> Kozłowski and March,<sup>14</sup> etc. (for a detailed review of these

developments, see Ludeña and López-Boada<sup>15</sup>). The initial formulation of LS-DFT was presented in the works of Petkov, Stoitsov, and Kryachko<sup>16–20</sup> and of Kryachko and Ludeña.<sup>1,2,21–26</sup> Some early applications of LS-DFT can be found in the works of Koga, Yamamoto, Ludeña, and Kryachko.<sup>27–39</sup> More recent applications and developments are discussed in the works of Ludeña, Kryachko, López-Boada, Valderrama, Maldonado, Pino, Karasiev, Hinze, Koga, and Colle.<sup>3,15,40–51</sup> Other more mathematically oriented developments on density transformations have been put forward by Bokanowski and Grébert<sup>52–54</sup> and, alternative formulations employing local-scaling transformations, by Pavlov et al.<sup>55,56</sup>

For completeness, let us also mention the work of Freed and Levy<sup>57</sup> where the problem is posed of how to convert the exact ground-state density,  $\rho_0(\vec{r})$ , for an external potential,  $v(\vec{r})$ , into the ground-state density,  $\rho(\vec{r})$ , of another system with external potential,  $v(\vec{r}) + \lambda(\vec{r})$  [where  $\lambda(\vec{r})$  is a “driving” potential]. This work leads to an integral equation relating  $\rho_0(\vec{r})$  and  $\rho(\vec{r})$  (via the density–density correlation function) which, in general terms, may be interpreted as a density transformation akin to those just discussed.

In the present work, we survey applications of LS-DFT to atoms and diatomic molecules. In the second section, using a simple basis set formed by generalized Slater-type orbitals for the  $1s$ ,  $2s$ ,  $3s$ ,  $2p$ , and  $3p$  orbitals, we are able to extend to second-row atoms the derivation<sup>50</sup> of explicit energy functionals. We illustrate the form of these functionals for the particular case of the aluminum atom. Because, in the present treatment, emphasis is placed in the symmetry problem, namely, in the problem of how to construct energy–density functionals that incorporate the spin and angular momentum characteristics of a particular spectroscopic term (and, hence, of its corresponding wave function), we discuss, in the third section, the construction of density functionals for the  $^1S$ ,  $^3P$ , and  $^1D$  multiplets of the  $1s^2 2s^2 2p^2$  configuration

of carbon at the Hartree–Fock and Kohn–Sham *x-only* levels. In the fourth section, we analyze the decomposition of the correlation energy into its dynamical and nondynamical components and introduce the concept of a reference wave function. The latter allows us to distinguish between “long-range” and “short-range” correlation. In the fifth section, we advance a cluster expansion procedure for the treatment of the dynamical component of the “short-range” part of the correlation energy. The sixth section deals with some aspects of density transformations for diatomic molecules. In the seventh section, we examine the improvement brought about by these density transformations on approximate single Slater determinant wave functions for diatomic molecules. We also apply these transformations to the Kohn–Sham *x-only* problem for these systems. In the eighth section we discuss some possible extensions of LS-DFT to the treatment of polyatomic molecules and solids. Finally, in the last section, we present some conclusions.

## Hartree–Fock Energy–Density Functionals for First- and Second-Row Atoms

### ISOTROPIC LOCAL-SCALING TRANSFORMATIONS

We briefly deal here with some relevant aspects of local-scaling transformations, because, in what follows, we rely heavily on some of the definitions introduced in this subsection.

Isotropic local-scaling transformations modify the vector  $\vec{r}$  at each point of  $\mathcal{R}^3$  according to:

$$\vec{f}(\vec{r}) = \lambda(\vec{r})\vec{r} = (\lambda(\vec{r})x, \lambda(\vec{r})y, \lambda(\vec{r})z) \quad (1)$$

These transformations (for details see refs. 1 and 15), are isotropic because they locally scale all Cartesian coordinates by the same function,  $\lambda(\vec{r})$  (in Appendix B, we deal with nonisotropic transformations). They keep the direction of the transformed vector  $\vec{f}(\vec{r})$  constant and satisfy, as all density transformations, the following equation relating an initial or “generating” density  $\rho_g(\vec{r})$  and a final density  $\rho(\vec{r})$ :

$$\rho(\vec{r}) = J(\vec{f}(\vec{r}); \vec{r}) \rho_g(\vec{f}(\vec{r})) \quad (2)$$

where  $J(\vec{f}(\vec{r}); \vec{r})$  is the Jacobian. For isotropic trans-

formations the Jacobian is:

$$J(\lambda(\vec{r})\vec{r}; \vec{r}) = \begin{vmatrix} \frac{\partial \lambda(\vec{r})x}{\partial x} & \frac{\partial \lambda(\vec{r})y}{\partial x} & \frac{\partial \lambda(\vec{r})z}{\partial x} \\ \frac{\partial \lambda(\vec{r})x}{\partial y} & \frac{\partial \lambda(\vec{r})y}{\partial y} & \frac{\partial \lambda(\vec{r})z}{\partial y} \\ \frac{\partial \lambda(\vec{r})x}{\partial z} & \frac{\partial \lambda(\vec{r})y}{\partial z} & \frac{\partial \lambda(\vec{r})z}{\partial z} \end{vmatrix} = \lambda^3(\vec{r})[1 + \vec{r} \cdot \nabla_{\vec{r}} \ln \lambda(\vec{r})] \quad (3)$$

From eqs. (2) and (3) we obtain the following expression for  $\lambda(\vec{r})$ :

$$\lambda(\vec{r}) = \left[ \frac{\rho(\vec{r})}{\rho_g(\lambda(\vec{r})\vec{r})(1 + \vec{r} \cdot \nabla_{\vec{r}} \ln \lambda(\vec{r}))} \right]^{1/3} \quad (4)$$

Eq. (4) is a first-order differential equation for the transformation function,  $\lambda(\vec{r})$ . Introducing the function,  $f(\vec{r})$ , by means of the following equivalence:

$$\lambda(\vec{r}) = \frac{f(\vec{r})}{r} \quad (5)$$

we can rewrite eq. (4) as:

$$\frac{\rho(\vec{r})}{\rho_g(\vec{f}(\vec{r}))} = \frac{1}{r^3} \vec{r} \cdot \nabla_{\vec{r}} f^3(\vec{r}) \quad (6)$$

These transformations can be used to generate from an initial orbital set,  $\{\phi_{g,k}^{[i]}(\vec{r})\}_{k=1}^N$ , a new set of transformed orbitals:

$$\begin{aligned} \phi_{p,k}^{[i]}(\vec{r}) &= \hat{f} \phi_{g,k}^{[i]}(\vec{r}) = \left[ J(\vec{f}(\vec{r}); \vec{r}) \right]^{1/2} \phi_{g,k}^{[i]}(\vec{f}(\vec{r})) \\ &= \left[ \frac{\rho(\vec{r})}{\rho_g^{[i]}(\vec{f}(\vec{r}))} \right]^{1/2} \phi_{g,k}^{[i]}(\vec{f}(\vec{r})) \end{aligned} \quad (7)$$

For the case of spherically symmetric, or spherically averaged densities:

$$\rho(r) = \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \rho(r, \theta, \phi) \quad (8)$$

$$\rho_g(f) = \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \rho_g(f, \theta, \phi) \quad (9)$$

the local-scaling function  $\lambda(r, \theta, \phi)$  reduces to  $\lambda(r)$  and eq. (6) becomes:

$$\frac{df(r)}{dr} = \frac{r^2}{f^2(r)} \frac{\rho(r)}{\rho_g(f(r))} \quad (10)$$

and the scaling function  $\lambda(r)$  is given by:

$$\lambda(r) = \frac{f}{r} = \left( \frac{\rho(r)}{\rho_g(f)} \right)^{1/3} \{1 + \vec{r} \cdot \nabla_{\vec{r}} \ln \lambda(r)\}^{-1/3} \quad (11)$$

From eqs. (10) and (11) we obtain the chain rule:

$$\begin{aligned} \frac{d}{dr} &= \left( \frac{df}{dr} \right) \frac{d}{df} \\ &= \left( \frac{\rho(r)}{\rho_g(f)} \right)^{1/3} \{1 + \vec{r} \cdot \nabla_{\vec{r}} \ln \lambda(r)\}^{2/3} \cdot \frac{d}{df} \end{aligned} \quad (12)$$

Because for atoms we assume a separation between radial and angular functions [eq. (22)], these transformations affect only the radial part of the “generating” orbitals:

$$\begin{aligned} R_{\rho, n_i l_i}(r) &= \left( \frac{df}{dr} \right)^{1/2} \left( \frac{f}{r} \right) R_{g, n_i l_i}(f) \\ &= \sqrt{\frac{\rho(r)}{\rho_g(f)}} R_{g, n_i l_i}(f) \end{aligned} \quad (13)$$

### HARTREE-FOCK PROBLEM EXPRESSED IN TERMS OF LOCALLY SCALED ORBITALS

Consider a single Slater determinant formed from the set  $\{\phi_{\rho, k}^{[i]}(\vec{r})\}$  of locally scaled one-particle orbitals [defined in eq. (7)]:

$$\begin{aligned} \Phi_{\rho}^{[i]}(\vec{r}_1, s_1, \dots, \vec{r}_N, s_N) \\ \equiv \frac{\det}{\sqrt{N!}} \left[ \phi_{\rho, 1}^{[i]}(\vec{r}_1) \sigma_{m_{s_1}}(s_1) \dots \right. \\ \left. \phi_{\rho, N}^{[i]}(\vec{r}_N) \sigma_{m_{s_N}}(s_N) \right] \end{aligned} \quad (14)$$

where the spin functions are denoted by  $\sigma_{m_{s_k}}(s_k)$ . The superscript  $[i]$  labels the different “orbits”  $\mathcal{O}_{\mathcal{S}}^{[i]}$  associated with these sets. By an “orbit” we mean the subclass  $\mathcal{O}_{\mathcal{S}}^{[i]}$  of the class  $\mathcal{S}_N$  of single Slater determinants where this subclass is generated by means of eq. (14) by isotropic local-scaling of the initial (fixed) orthonormal set  $\{\phi_{g, k}^{[i]}(\vec{r})\}_{k=1}^N$ , according to eq. (7). (If the initial set depends on

parameters, these must be fixed as different “orbits” are produced by different sets of parameters.) Clearly, for each such an initial orbit set, because  $\rho$  spans the set  $\mathcal{N}_{\Phi}$  (of all admissible densities), an infinite subclass of Slater determinants is generated (which is closed under the action of the continuous group of local-scaling transformations<sup>1,2</sup>).

In the context of LS-DFT, the Hartree-Fock variational principle is<sup>58</sup>:

$$E_0^{HF} = \inf_{\substack{\text{over all orbits} \\ \mathcal{O}_{\mathcal{S}}^{[i]} \subset \mathcal{S}_N}} \left\{ \inf_{\substack{\rho(\vec{r}) \in \mathcal{N}_{\Phi} \\ \Phi_{\rho}^{[i]} \in \mathcal{O}_{\mathcal{S}}^{[i]}}} \left\{ E[\Phi_{\rho}^{[i]}] \right\} \right\} \quad (15)$$

In eq. (15),  $E[\Phi_{\rho}^{[i]}]$  is the expectation value of  $\Phi_{\rho}^{[i]}$  with respect to the many-particle Hamiltonian. This functional can also be written as a functional of the one-particle density,  $\rho$ , and the wave function,  $\Phi_g^{[i]}$ , formed from the initial orbitals. Thus, we have the one-to-one correspondence between a functional of a wave function and a functional of the one-particle density:

$$E[\Phi_{\rho}^{[i]}] = \mathcal{E}[\rho, \Phi_g^{[i]}] \quad (16)$$

Now, because we can always fix an arbitrary initial function,  $\Phi_g^{[i]}$ , it is clear that the right-hand side of eq. (16) is just a functional of the one-particle density,  $\rho$ , although its particular form depends on the initial function (a particularly simple choice based on generalized Slater-type orbitals is shown below to lead to quite accurate results).

The functional  $\mathcal{E}[\rho, \Phi_g^{[i]}]$  can be written in terms of the kinetic-, Coulomb-, exchange-, and external-energy components:

$$\begin{aligned} \mathcal{E}[\rho, \Phi_g^{[i]}] &= T[\rho, \Phi_g^{[i]}] + \frac{1}{2} \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \\ &\times \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \int d^3 \vec{r} \rho(\vec{r}) v(\vec{r}) \\ &+ E_x[\rho, \Phi_g^{[i]}] \end{aligned} \quad (17)$$

where the kinetic energy functional is:

$$\begin{aligned} T[\rho, \Phi_g^{[i]}] &= \frac{1}{2} \sum_{s_1} \int d^3 \vec{r}_1 \nabla_{\vec{r}_1} \nabla_{\vec{r}_1'} \\ &\times D_{\rho}^{[i]}(\vec{r}_1, s_1; \vec{r}_1', s_1') \Big|_{\vec{r}_1' = \vec{r}_1; s_1' = s_1} \end{aligned} \quad (18)$$

and the exchange-energy functional is:

$$\begin{aligned}
 E_x[\rho, \Phi_g^{[i]}] &= -\frac{1}{2} \sum_{s_1} \int d^3\vec{r}_1 \sum_{s_2} \int d^3\vec{r}_2 \\
 &\times \frac{D_\rho^{[i]}(\vec{r}_1, s_1; \vec{r}_2, s_2) D_\rho^{[i]}(\vec{r}_2, s_2; \vec{r}_1, s_1)}{|\vec{r}_1 - \vec{r}_2|} \quad (19)
 \end{aligned}$$

The spin-dependent 1-matrix appearing in these expressions is defined by:

$$\begin{aligned}
 D_\rho^{[i]}(\vec{r}_1, s_1; \vec{r}_2, s_2) &= \sum_{k=1}^N \phi_{\rho,k}^{[i]*}(\vec{r}_1) \sigma_{m_{s_k}}(s_1) \phi_{\rho,k}^{[i]}(\vec{r}_2) \sigma_{m_{s_k}}(s_2) \quad (20)
 \end{aligned}$$

and its corresponding one-particle density, by:

$$\rho(\vec{r}) = \sum_{k=1}^N |\phi_{\rho,k}^{[i]}(\vec{r})|^2 \quad (21)$$

## KINETIC AND EXCHANGE-ENERGY ATOMIC FUNCTIONALS

For atoms, we can separate the radial and angular parts so that the locally scaled atomic orbital is given by:

$$\phi_{\rho,i}(\vec{r}) = R_{\rho, n_i l_i}(r) Y_{l_i, m_{l_i}}(\theta, \phi) \quad (22)$$

where we have assumed that the local-scaling transformation only affects the radial function (for an alternative and more general transformation, see Appendix B). Substituting eq. (22) into eq. (18), integrating over the angular coordinates and using eqs. (10)–(12) we arrive, after some straightforward algebra, to the following expression for the kinetic energy functional (for simplicity we drop the “orbit” superindex):

$$\begin{aligned}
 T[\rho, \Phi_g] &= T_W[\rho] + \int_0^\infty dr r^2 p^{5/3}(r) \\
 &\times \left[ (1 + \vec{r} \cdot \nabla \ln \lambda(r))^{4/3} \tau_N \right. \\
 &\left. + (1 + \vec{r} \cdot \nabla \ln \lambda(r))^{-2/3} \kappa_N \right] \quad (23)
 \end{aligned}$$

Here,  $T_W[\rho]$  is the Weizsäcker kinetic energy functional<sup>59</sup>:

$$T_W[\rho] = \frac{1}{8} \int_0^\infty dr r^2 \frac{(\nabla \rho(r))^2}{\rho(r)} \quad (24)$$

and  $\tau_N$  and  $\kappa_N$  are radial and the angular kinetic energy modulating factors defined by:

$$\begin{aligned}
 \tau_N &= \frac{1}{\rho_g^{8/3}(f)} \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[ R_{g, n_i l_i}(f) \frac{dR_{g, n_j l_j}(f)}{df} \right. \\
 &\left. - R_{g, n_j l_j}(f) \frac{dR_{g, n_i l_i}(f)}{df} \right]^2 \quad (25)
 \end{aligned}$$

and:

$$\kappa_N = \frac{1}{\rho_g^{5/3}(f)} \sum_{i=1}^N \frac{l_i(l_i + 1)}{2} \left( \frac{R_{g, n_i l_i}(f)}{f} \right)^2 \quad (26)$$

Similarly, the exchange-energy functional becomes:

$$\begin{aligned}
 E_x[\rho, \Phi_g] &= -\frac{1}{2} \int_0^\infty dr_1 r_1^2 \sum_{k=0}^{k_{max}} \rho(r_1)^{(4+k)/3} \\
 &\times \left( \frac{1}{1 + \vec{r}_1 \cdot \nabla_{\vec{r}} \ln \lambda(r_1)} \right)^{(k+1)/3} \chi_N^k(f_1) \quad (27)
 \end{aligned}$$

where  $k_{max}$  is determined by the triangular condition.<sup>60</sup> Again, we see that there arises an angular-momentum-dependent exchange-modulating factor:

$$\begin{aligned}
 \chi_N^k(f_1) &= \frac{1}{f^{k+1} \rho_g(f_1)^{(4+k)/3}} \sum_{i=1}^N \sum_{j=1}^N \delta(m_{s_i}, m_{s_j}) \\
 &\times b^k(l_i, m_{l_i}; l_j, m_{l_j}) G_{ij}^k(f_1) \quad (28)
 \end{aligned}$$

where  $G_{ij}^k(f_1)$  is defined by:

$$\begin{aligned}
 G_{ij}^k(f_1) &= 2 R_{g, n_i l_i}(f_1) R_{g, n_j l_j}(f_1) \int_0^{f_1} df_2 \\
 &\times f_2^2 r_2^k(f_2) R_{g, n_i l_i}(f_2) R_{g, n_j l_j}(f_2) \quad (29)
 \end{aligned}$$

and  $b^k(l_i, m_{l_i}; l_j, m_{l_j}) = [c^k(l_i, m_{l_i}; l_j, m_{l_j})]^2$  is the angular coefficient appearing in the usual exchange integrals.<sup>60</sup>

Let us comment on these functionals. First, we observe that the kinetic energy functional has two components: the Weizsäcker term plus a generalized Thomas–Fermi term. The latter contains the usual universal factor,  $\rho^{5/3}$ , in agreement with the usual expression for this term in DFT. But, in

addition, let us remark that there appear two extra terms:  $(1 + \vec{r} \cdot \nabla \ln \lambda(r))^{4/3} \tau_N$  and  $(1 + \vec{r} \cdot \nabla \ln \lambda(r))^{-2/3} \kappa_N$ . Moreover, when we take the generating radial orbitals to be plane waves of the form  $R_{g,k}(r) = \sqrt{3/4\pi} \exp(2\pi i(k - (N + 1)/2)r^3/3)$ , then the initial density becomes  $\rho_g(r) = \sum_{k=1}^N R_{g,k}^*(r) R_{g,k}(r) = (3/4\pi)N$ . If we approximate the local-scaling function by  $\lambda(r) \simeq (\rho(r)/\rho_g(r))^{1/3}$  and the value of  $r$  by that of the Fermi radius  $r \simeq r_s = (3/4\pi)\rho^{-1/3}$ , then we obtain  $(1 + \vec{r} \cdot \nabla \ln \lambda(r)) \simeq (1 + (1/4\pi) \nabla \rho / \rho^{4/3})$ . Thus, we see that terms that are used in standard DFT also arise in a very natural way in the present formulation. The difference, however, stems from the modulating factors particular to each physical system. We provide an approximate representation of these terms in the following subsection.

For completeness, we mention an early effort by Dawson and March<sup>61</sup> (based on methods quite distinct from those employed here) that also led to an explicit kinetic energy functional containing the Weizsäcker term plus a correction involving the Thomas–Fermi factor.

### MODULATING FACTORS IN GENERALIZED SLATER-TYPE ORBITAL BASIS

Let us consider now an explicit realization of the modulating factors appearing in the kinetic-energy and exchange-energy functionals. For this purpose, we introduce the following generalized Slater-type orbitals:

$$R_{g,1s}(r) \equiv N_{1s} \exp(-\alpha_{1s} r^\beta) \quad (30)$$

$$R_{g,2s}(r) \equiv N_{2s} (1 + B_{2s} r) \exp(-\alpha_{2s} r^\beta) \quad (31)$$

$$R_{g,3s}(r) \equiv N_{3s} (1 + B_{3s} r + C_{3s} r^2) \exp(-\alpha_{3s} r^\beta) \quad (32)$$

$$R_{g,2p}(r) \equiv N_{2p} r \exp(-\alpha_{2p} r^\beta) \quad (33)$$

$$R_{g,3p}(r) \equiv N_{3p} (1 + B_{3p} r) r \exp(-\alpha_{3p} r^\beta) \quad (34)$$

where the normalization constants are given by:

$$N_{1s} = (\beta)^{1/2} (2\alpha_{1s})^{3/(2\beta)} \tilde{\Gamma}(3)^{-1/2} \quad (35)$$

$$N_{2s} = (\beta)^{1/2} (2\alpha_{2s})^{3/(2\beta)} \left( \tilde{\Gamma}(3) + \frac{2B_{2s}}{(2\alpha_{2s})^{1/\beta}} \tilde{\Gamma}(4) + \frac{B_{2s}^2}{(2\alpha_{2s})^{2/\beta}} \tilde{\Gamma}(5) \right)^{-1/2} \quad (36)$$

$$N_{3s} = (\beta)^{1/2} (2\alpha_{3s})^{3/(2\beta)} \left( \tilde{\Gamma}(3) + \frac{2B_{3s}}{(2\alpha_{3s})^{1/\beta}} \tilde{\Gamma}(4) + \frac{2C_{3s} + B_{3s}^2}{(2\alpha_{3s})^{2/\beta}} \tilde{\Gamma}(5) + \frac{2B_{3s}C_{3s}}{(2\alpha_{3s})^{3/\beta}} \tilde{\Gamma}(6) + \frac{C_{3s}^2}{(2\alpha_{3s})^{4/\beta}} \tilde{\Gamma}(7) \right)^{-1/2} \quad (37)$$

$$N_{2p} = (\beta)^{1/2} (2\alpha_{2p})^{5/(2\beta)} \tilde{\Gamma}(5)^{-1/2} \quad (38)$$

$$N_{3p} = (\beta)^{1/2} (2\alpha_{3p})^{5/(2\beta)} \left( \tilde{\Gamma}(5) + \frac{2B_{3p}}{(2\alpha_{3p})^{1/\beta}} \tilde{\Gamma}(6) + \frac{B_{3p}^2}{(2\alpha_{3p})^{4/\beta}} \tilde{\Gamma}(7) \right)^{-1/2} \quad (39)$$

The orthogonalization parameters are:

$$B_{2s} = -A_{12} \frac{\tilde{\Gamma}(3)}{\tilde{\Gamma}(4)}, \quad B_{3s} = \frac{a}{c}, \quad C_{3s} = \frac{b}{c}, \quad (40)$$

$$B_{3p} = -(\alpha_{2p} + \alpha_{3p})^{1/\beta} \frac{\tilde{\Gamma}(5)}{\tilde{\Gamma}(6)}$$

where:

$$a = (A_{23}^3 - A_{12} A_{23}^2 - A_{13}^2 A_{23}) \tilde{\Gamma}(3) \tilde{\Gamma}(4) \tilde{\Gamma}(5) + A_{12} A_{13}^2 \tilde{\Gamma}(3)^2 \tilde{\Gamma}(6) \quad (41)$$

$$b = (A_{13}^2 A_{23}^2 - A_{13} A_{23}^3 + A_{12} A_{13} A_{23}^2) \times \tilde{\Gamma}(3) \tilde{\Gamma}(4)^2 \tilde{\Gamma}(5) - A_{23} A_{13}^2 \tilde{\Gamma}(3)^2 \tilde{\Gamma}(5) \quad (42)$$

$$c = (A_{23} A_{13} - A_{23}^2) \tilde{\Gamma}(4)^2 \tilde{\Gamma}(5) - A_{12} A_{13} \tilde{\Gamma}(3) \tilde{\Gamma}(4) \tilde{\Gamma}(6) + A_{12} A_{23} \tilde{\Gamma}(3) \tilde{\Gamma}(5)^2 \quad (43)$$

In the above expressions  $A_{ij} \equiv (\alpha_{is} + \alpha_{js})^{1/\beta}$  and we have used the Gamma function:

$$\tilde{\Gamma}(k) \equiv \Gamma(k/\beta) = \int_0^\infty r^{k/\beta-1} e^{-r} dr \quad (44)$$

The emphasis we have placed in writing in detail the generalized Slater-type orbitals stems from the fact that, once they are known, it is then possible to insert them into eqs. (25), (26), (28), and (29) to obtain explicit analytical expressions for the modulating factors  $\tau_N$ ,  $\kappa_N$ , and  $\chi_N$ , respectively. This, in turn, allows us to express the kinetic energy and exchange-energy functionals as explicit functionals of the transformation function,  $f[\rho]$ ;

$r$ ). The final step for the purpose of converting these expressions into *bona fide* functionals of the one-particle density  $\rho$  is achieved when  $f([\rho]; r)$  is written as an explicit function of  $\rho$ . As indicated in Appendix A, this is possible by using a Padé approximant for  $f([\rho]; r)$ . There is also the alternative option of computing  $f([\rho]; r)$  numerically and of carrying out a fully numerical evaluation of these functionals.

Calculations of first-row atoms<sup>50</sup> and second-row atoms have been performed using the functionals just described. We present numerical results obtained by employing a modified version of the numerical program for atoms of Froese-Fischer.<sup>62</sup> In Table I, we list the optimal parameters for the generalized Slater-type orbitals for the atoms considered. In Table II we list the kinetic, exchange, and total energies and compare them with the corresponding Hartree–Fock and the optimized effective potential (OEP) values.<sup>63,64</sup> For completeness, we have also included the total energy values for  $\beta = 1$  as these correspond to the single- $\zeta$  approximation.<sup>65</sup> The exchange energies listed are calculated with spherical averaging.<sup>66</sup> Let us remark that our present results are *strict upper bounds* to the Hartree–Fock energies (for this reason, they are listed with the same number of decimals as the Hartree–Fock values).

We may conclude from Table II that the LS-DFT exchange energy functionals approach quite closely

the corresponding Hartree–Fock ones. In fact, the difference in exchange energy, in all the cases treated here, is of the order of millihartrees or even less. There is a larger discrepancy in the kinetic energy values as the difference between the LS-DFT and the Hartree–Fock values can get as large as 0.1 hartree (e.g., in the case of Ar). Even though this discrepancy may seem large, let us remark that the LS-DFT kinetic energy functionals are quite accurate when compared with other DFT kinetic energy functionals (see, e.g., ref. 67).

For completeness we have also included in Table II the OEP total energy values.<sup>63</sup> It is observed that these values are closer to the Hartree–Fock ones than the corresponding LS-DFT energies. Let us remark, however, that the OEP values are obtained by means of a minimization process that involves the iterative solution of one-particle equations and that, in this sense, it is a method that shares many of the characteristics of the Hartree–Fock approximation (although, in the spirit of DFT, the potential is local). In the present case, the LS-DFT energies are obtained from explicit functionals, which contain, as variational parameters,  $\{\alpha_i\}$  and  $\beta$ . As shown elsewhere, when we use for first-row atoms a set  $\{\beta_i\}$ , we obtain values that are practically undistinguishable from the OEP ones,<sup>50</sup> but in this case it is not possible to obtain explicit analytic expressions for the functionals because some integrals cannot be calculated analyti-

**TABLE I.**   
Optimal Parameters for First- and Second-Row Atoms, Obtained by Total Energy Minimization at Fixed Hartree–Fock Density.

Atom	$\beta$	$\alpha_{1s}$	$\alpha_{2s}$	$\alpha_{2p}$	$\alpha_{3s}$	$\alpha_{3p}$
Li	1.3157825	2.8899787	0.7740376			
Be	1.2830233	3.7887969	1.1384741			
B	1.2364493	4.7490824	1.5450085	1.1335431		
C	1.2215390	4.8816194	1.6506443	1.2569718		
N	1.2158897	5.7242261	1.9790775	1.5416808		
O	1.2217844	7.2803221	2.5567004	1.9873090		
F	1.2241614	7.4238354	2.6376399	2.0592196		
Ne	1.2250371	8.1773320	2.9313392	2.3019566		
Na	1.2040370	13.202776	4.8802257	3.9808032	1.7143683	
Mg	1.1923686	12.499611	4.7227302	3.9550571	1.8939674	
Al	1.1818711	12.119422	4.6664920	3.9915056	2.0546467	1.4906124
Si	1.1748590	11.780835	4.6031178	4.0032502	2.1386973	1.6379375
P	1.1695742	11.568262	4.5756578	4.0317438	2.2029200	1.7478119
S	1.1656644	12.765931	5.1003719	4.5420844	2.5334360	2.0408092
Cl	1.1619650	10.897381	4.3945170	3.9459412	2.2339002	1.8284340
Ar	1.1576955	15.205220	6.1884490	5.5924571	3.2051485	2.6606547

**TABLE II.**  
**Total, Kinetic, and Exchange Energies for Ground States of Neutral Atoms. Hartree–Fock and OEP Values**  
**Included for Comparison (Hartrees).**

Atom	$-E_{Total}^a$	$-E_{Total}^{LS-DFT}$	$-E_{Total}^{OEP^b}$	$-E_{Total}^{HF} = T^{HFC}$	$T^{LS-DFT}$	$-E_x^{OEP^d}$	$-E_x^{LS-DFT^e}$	$-E_x^{HFe}$
Li	7.4184820	7.4326353	7.43250	7.4327269	7.4328807	1.781	1.781249	1.781186
Be	14.556740	14.572470	14.57243	14.573023	14.573610	2.666	2.666947	2.666914
B	24.498370	24.527667	24.52834	24.529061	24.529620		3.742962	3.743797
C	37.622389	37.686695	37.68891	37.688619	37.689194		5.014164	5.015232
N	54.268899	54.398488	54.40340	54.400934	54.401827	6.604	6.489698	6.490722
O	74.540362	74.805922	74.81208	74.809399	74.812503		8.134316	8.134839
F	98.942114	99.402954	99.40922	99.409349	99.415044		10.00273	10.00343
Ne	127.81219	128.53684	128.5454	128.54710	128.55594	12.105	12.10693	12.10835
Na	161.12392	161.84417	161.8566	161.85893	161.87344	14.013	14.01732	14.01752
Mg	198.85779	199.58802	199.6116	199.61464	199.64127	15.988	15.99431	15.99429
Al	241.15376	241.84121	241.8733	241.87671	241.91185		18.06924	18.06960
Si	288.08997	288.80725	288.8507	288.85436	288.90071		20.25960	20.26027
P	339.90989	340.65832	340.7150	340.71878	340.77786	22.634	22.56907	22.57008
S	396.62761	397.42942	397.5016	397.50490	397.57908		24.97405	24.97531
Cl	458.52370	459.39162	459.4776	459.48207	459.57038		27.50947	27.51161
Ar	525.76526	526.71369	526.8122	526.81751	526.91757	30.175	30.18118	30.18494

<sup>a</sup> Ref. 65. These are the single- $\zeta$  calculations corresponding to the  $\beta = 1$  nonscaled orbitals [eqs. (30)–(34)]. <sup>b</sup> Ref. 63. <sup>c</sup> These quantities are equal up to digits quoted. <sup>d</sup> Ref. 64. <sup>e</sup> The exchange energy for open-shell atoms was calculated by averaging over the possible ways of occupying the magnetic states of the open shells, which is equivalent to carrying out a spherical averaging (see, e.g., ref. 66).

cally. Thus, we stress the fact that the LS-DFT values reported here are the closest approximations to Hartree–Fock values available in the literature for *explicit* DFT functionals.

Of particular importance is the fact that the present functionals lead in a natural way to atomic shell structure. Crucial in this respect is the effect of the modulating factors, and, in particular, of  $\tau_N$ . For this reason, in what follows we consider in some detail the term  $\tau_N$  corresponding to the  $^2P$  state of the aluminum atom. This term consists of six microstates. We select arbitrarily the microstate with  $M_S = 1/2$  and  $M_L = 0$  with configuration  $1s^2 2s^2 2p^6 3s^2 3p_0^\alpha$ .

The explicit expression for the modulating factor,  $\tau$ , of aluminum is given by:

$$\tau = \{\tau_{KL} + \tau_{KM} + \tau_{LL} + \tau_{LM} + \tau_{MM}\} \quad (45)$$

where we have collected the terms corresponding to each atomic shell and intershell. These terms are defined by:

$$\begin{aligned} \tau_{IJ} &= \frac{1}{2\rho_g^{8/3}(f)} \omega_{IJ} \\ \omega_{KL} &= 4W_{1s2s} + 12W_{1s2p} \\ \omega_{KM} &= 4W_{1s2s} + 2W_{1s3p} \end{aligned} \quad (46)$$

$$\begin{aligned} \omega_{LL} &= 12W_{2s2p} \\ \omega_{LM} &= 4W_{2s3s} + 2W_{2s3p} + 4W_{2p3s} + 6W_{2p3p} \\ \omega_{MM} &= 2W_{3s3p} \end{aligned}$$

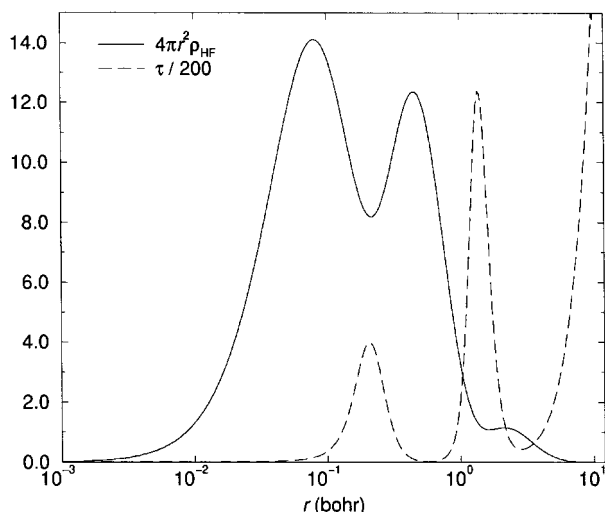
where:

$$W_{ij} = \left( R_{g,n_i,l_i}(f) \frac{dR_{g,n_j,l_j}(f)}{df} - R_{g,n_j,l_j}(f) \frac{dR_{g,n_i,l_i}(f)}{df} \right)^2 \quad (47)$$

In Figure 1, we compare  $4\pi r^2 \rho_{HF}(r)$  for aluminum with  $\tau$  (downscaled by a factor of 200). The remarkable fact is that the first and second maxima of  $\tau$  are placed precisely at the first and second minima, respectively, of the radial distribution, namely, at the intershell boundaries. In the outer region,  $\tau$  goes to infinity rather sharply. It is clear from Figure 1 that the kinetic energy modulating factor is responsible for the formation of sharply defined potential basins coinciding with the atomic shells. But, also, in a reverse sense, the modulating factor,  $\tau$ , is implicitly determined by the local and global minima of the radial distribution.

The behavior of the different shell and intershell components of  $\tau$  are given in Figures 2 and 3. It is

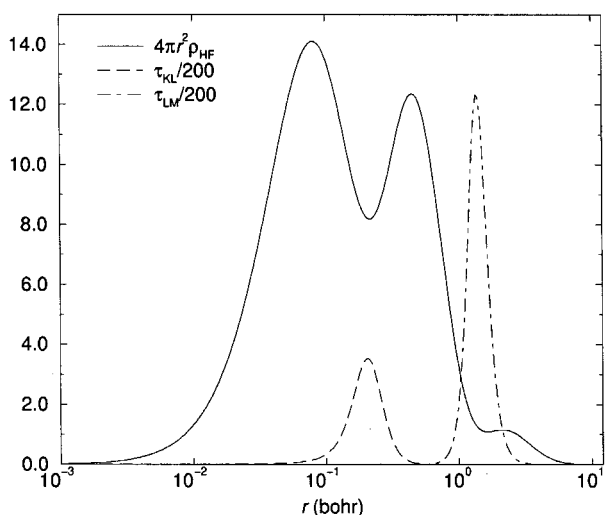




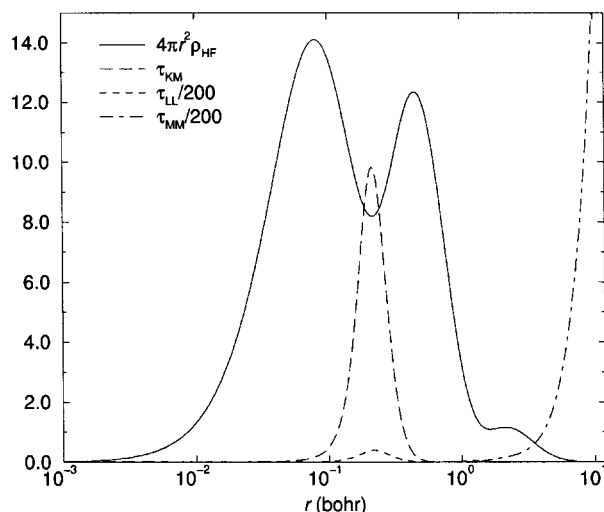
**FIGURE 1.** Hartree-Fock density and modulating factor for the ground state of the Al atom.

observed that the first maximum is almost entirely given by  $\tau_{KL}$ . Similarly, the second maximum is accounted for by  $\tau_{LM}$ . The contribution of  $\tau_{KM}$  is practically zero and that of  $\tau_{LL}$  is negligible. On the other hand, the sharp pick-up of  $\tau$  in the outer region is due to the contribution  $\tau_{MM}$ .

The point of the previous analysis is to discriminate among the relative importance levels of the various components to the modulating factor with a view toward introducing simpler approxima-



**FIGURE 2.** Hartree-Fock density and KL and LM components of the modulating factor,  $\tau$ , for the ground state of the Al atom.



**FIGURE 3.** Hartree-Fock density and KM, LL, and MM components of the modulating factor,  $\tau$ , for the ground state of the Al atom.

tions expressed as functions of the density and perhaps even as functions that are “universal” for some classes of systems. Work along in this area is currently under way.

## Symmetry Problem in Atoms: Explicit Energy Functionals for Multiplets

One of the most challenging problems in density functional theory has to do with how to extend DFT to deal with multiplicities arising from spin and angular momentum restrictions on atomic and molecular systems. A number of investigators have considered this problem in the context of the Hohenberg-Kohn-Sham version of DFT.<sup>68–77</sup> We discuss, in this section, how this problem can be successfully treated in the context of LS-DFT.

The Hamiltonian operator,  $\hat{H}$ , for atoms commutes with the total angular momentum operators,  $\hat{L}^2$  and  $\hat{L}_Z$ , with the total spin operators,  $\hat{S}^2$  and  $\hat{S}_Z$ , and with the parity operator,  $\hat{\pi}$ . This property implies that the eigenfunctions of  $\hat{H}$  must be simultaneous eigenfunctions of all these operators. This condition has consequences on the structure of the 1-matrix and, hence, on the energy density functionals just discussed.

To illustrate the restrictions that angular momentum and spin introduce in density functionals, we discuss in what follows the particular case of

the carbon atom at the restricted Hartree–Fock level and construct explicit functionals for its multiplets.

Consider the configuration  $1s^2 2s^2 2p^2$  for the carbon atom. Because of angular momentum and spin degeneracy there arise 15 microstates for this configuration. Since the differences in these microstates are due to the different couplings of  $2p$  orbitals with spin functions, we deal, for simplicity only, with  $2p^2$ . The 15 microstates for two equivalent  $2p$  orbitals are<sup>78</sup>:

$$\begin{aligned} \phi_1 &= (1^+ 0^+), & \phi_2 &= (1^+ 0^-), & \phi_3 &= (1^- 0^-), \\ \phi_4 &= (1^+ - 1^+), & \phi_5 &= (1^+ - 1^-), & \phi_6 &= (1^- 1^-), \\ \phi_7 &= (0^+ - 1^+), & \phi_8 &= (0^+ - 1^-), \\ \phi_9 &= (0^- - 1^-), & \phi_{10} &= (1^+ 1^-), & \phi_{11} &= (1^- 0^+), \\ \phi_{12} &= (1^- - 1^+), & \phi_{13} &= (0^- - 1^+), \\ \phi_{14} &= (-1^+ - 1^-), & \phi_{15} &= (0^+ 0^-) \end{aligned} \quad (48)$$

The nine functions corresponding to the  $^3P$  term are:

$$\begin{aligned} \psi_1 &= \phi_1, & \psi_2 &= \frac{1}{\sqrt{2}}(\phi_2 + \phi_{11}), & \psi_3 &= \phi_3 \\ \psi_4 &= \phi_4, & \psi_5 &= \frac{1}{\sqrt{2}}(\phi_5 + \phi_{12}), & \psi_6 &= \phi_6 \\ \psi_7 &= \phi_7, & \psi_8 &= \frac{1}{\sqrt{2}}(\phi_8 + \phi_{13}), & \psi_9 &= \phi_9 \end{aligned} \quad (49)$$

The five  $^1D$  microstates are:

$$\begin{aligned} \psi_{10} &= \phi_{10}, & \psi_{11} &= \frac{1}{\sqrt{2}}(\phi_2 - \phi_{11}), \\ \psi_{12} &= \frac{1}{\sqrt{6}}(\phi_5 - \phi_{12} + 2\phi_{15}) \\ \psi_{13} &= \frac{1}{\sqrt{2}}(\phi_8 - \phi_{13}), & \psi_{14} &= \phi_{14} \end{aligned} \quad (50)$$

The wave function for the  $^1S$  term is:

$$\psi_{15} = \frac{1}{\sqrt{3}}(\phi_5 - \phi_{12} - \phi_{15}) \quad (51)$$

The 1-matrices corresponding to each one of these wave functions are block diagonalized into its  $\alpha\alpha$  and  $\beta\beta$  components. Hence, the operator,  $D_\psi^1(\vec{r}, s; \vec{r}', s')$ , can be written in matrix form as

follows:

$$D^1(\vec{r}, s; \vec{r}', s') = (\overrightarrow{2p}(\vec{r}, s))^\dagger \mathbf{D}_\psi^1 \overrightarrow{2p}(\vec{r}', s') \quad (52)$$

where  $(\overrightarrow{2p}(\vec{r}, s))^\dagger$  is the row vector:

$$\begin{aligned} (\overrightarrow{2p}(\vec{r}, s))^\dagger &= (2p_1(\vec{r})\alpha(s), 2p_0(\vec{r})\alpha(s), \\ &2p_{-1}(\vec{r})\alpha(s), 2p_1(\vec{r})\beta(s), \\ &2p_0(\vec{r})\beta(s), 2p_{-1}(\vec{r})\beta(s)) \end{aligned} \quad (53)$$

$\overrightarrow{2p}(\vec{r}', s')$  is the transposed column vector, and  $\mathbf{D}_\psi^1$  is the spin-block-diagonalized 1-matrix

$$\mathbf{D}_\psi^1 = \begin{pmatrix} \mathbf{D}_\psi^{1\alpha\alpha} & 0 \\ 0 & \mathbf{D}_\psi^{1\beta\beta} \end{pmatrix} \quad (54)$$

The 1-matrices for the  $^3P$  multiplet are (those identically zero are not listed):

$$\begin{aligned} \mathbf{D}_{\psi_1}^{1\alpha\alpha} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\ \mathbf{D}_{\psi_2}^{1\alpha\alpha} &= \mathbf{D}_{\psi_2}^{1\beta\beta} = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\ \mathbf{D}_{\psi_3}^{1\beta\beta} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\ \mathbf{D}_{\psi_4}^{1\alpha\alpha} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ \mathbf{D}_{\psi_5}^{1\alpha\alpha} &= \mathbf{D}_{\psi_5}^{1\beta\beta} = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1/2 \end{pmatrix}, \\ \mathbf{D}_{\psi_6}^{1\beta\beta} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ \mathbf{D}_{\psi_7}^{1\alpha\alpha} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ \mathbf{D}_{\psi_8}^{1\alpha\alpha} &= \mathbf{D}_{\psi_8}^{1\beta\beta} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 1/2 \end{pmatrix}, \\ \mathbf{D}_{\psi_9}^{1\beta\beta} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned} \quad (55)$$

Those of the  $^1D$  term are:

$$\begin{aligned}
 \mathbf{D}_{\psi_{10}}^{1\alpha\alpha} &= \mathbf{D}_{\psi_{10}}^{1\beta\beta} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
 \mathbf{D}_{\psi_{11}}^{1\alpha\alpha} &= \mathbf{D}_{\psi_{11}}^{1\beta\beta} = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 \mathbf{D}_{\psi_{12}}^{1\alpha\alpha} &= \mathbf{D}_{\psi_{12}}^{1\beta\beta} = \begin{pmatrix} 1/6 & 0 & 0 \\ 0 & 4/6 & 0 \\ 0 & 0 & 1/6 \end{pmatrix}, \quad (56) \\
 \mathbf{D}_{\psi_{13}}^{1\alpha\alpha} &= \mathbf{D}_{\psi_{13}}^{1\beta\beta} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 1/2 \end{pmatrix} \\
 \mathbf{D}_{\psi_{14}}^{1\alpha\alpha} &= \mathbf{D}_{\psi_{14}}^{1\beta\beta} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}
 \end{aligned}$$

The 1-matrix corresponding to the  $^1S$  term is:

$$\mathbf{D}_{\psi_{15}}^{1\alpha\alpha} = \mathbf{D}_{\psi_{15}}^{1\beta\beta} = \begin{pmatrix} 1/3 & 0 & 0 \\ 0 & 1/3 & 0 \\ 0 & 0 & 1/3 \end{pmatrix} \quad (57)$$

From the above equations, we conclude, in the first place, that there are different densities for each one of the microstates associated with the spectroscopic terms. For instance, the density corresponding to the  $^1S$  wave function,  $\psi_{15}$ , is the spherically symmetric function

$$\rho_{\psi_{15}}^{\alpha\alpha}(\vec{r}) = \frac{1}{4\pi} R_{2p}^2(r) \quad (58)$$

whereas, the density for the  $M_S = 0$  and  $M_L = 0$  wave function  $\psi_5$  of the  $^3P$  term is:

$$\rho_{\psi_5}^{\alpha\alpha}(\vec{r}) = \frac{3}{8\pi} R_{2p}^2(r) \sin^2\theta \quad (59)$$

and that for the  $M_S = 0$  and  $M_L = 0$  wave function,  $\psi_{12}$ , of the  $^1D$  term is:

$$\rho_{\psi_{12}}^{\alpha\alpha}(\vec{r}) = \frac{1}{8\pi} R_{2p}^2(r) (\sin^2\theta + 4 \cos^2\theta) \quad (60)$$

Nevertheless, for the  $^3P$  ensemble operator:

$$\begin{aligned}
 D^2([{}^3P]\vec{r}_1, s_1, \vec{r}_2, s_2; \vec{r}'_1, s'_1, \vec{r}'_2, s'_2) \\
 = \frac{1}{9} \sum_{i=1}^9 |\psi_i(\vec{r}_1, s_1, \vec{r}_2, s_2)\rangle \langle \psi_i(\vec{r}'_1, s'_1, \vec{r}'_2, s'_2)| \quad (61)
 \end{aligned}$$

the ensemble 1-matrix becomes exactly that of the  $^1S$  term and is given by eq. (57) and, hence, the ensemble density becomes the spherically symmetric function of eq. (58). The same 1-matrix (57) is also found for the  $^1D$  ensemble operator:

$$\begin{aligned}
 D^2([{}^1D]\vec{r}_1, s_2, \vec{r}_2, s_2; \vec{r}'_1, s'_1, \vec{r}'_2, s'_2) \\
 = \frac{1}{5} \sum_{i=10}^{14} |\psi_i(\vec{r}_1, s_1, \vec{r}_2, s_2)\rangle \langle \psi_i(\vec{r}'_1, s'_1, \vec{r}'_2, s'_2)| \quad (62)
 \end{aligned}$$

In the second place, we observe that, for calculation of kinetic energy for the carbon atom (whose ground state is  $^3P$ ), it does not matter whether we use the ensemble 1-matrix or any one of the 1-matrices corresponding to the  $^3P$  microstates. The point is that, because the angular part is integrated out, we obtain the same kinetic energy functional for all microstates belonging to this term. In fact, any one of the microstates belonging to the  $^3P$ ,  $^1D$ , or  $^1S$  terms yield the same kinetic energy functional. Moreover, because the ensemble 1-matrices for the  $^3P$  and  $^1D$  terms are the same and are equal to the 1-matrix of the  $^1S$  state, it follows that the kinetic energy functional does not discriminate among microstates or ensembles (at least those with equal weights<sup>77</sup>).

In spite of the fact that all microstates and ensembles yield the same kinetic energy functional, they do not lead to the same kinetic energy value because the radial densities of the different multiplets are not equal. This point is illustrated in Table III, where we present several values for the kinetic energy of the carbon atom multiplets, evaluated by direct minimization of the total energy functional with the restriction—imposed by means of local-scaling transformations—that the minimizing orbitals yield the radial Hartree–Fock density of the particular multiplet.

The situation is quite different for the exchange-energy functional, where we observe that as a result of angular momentum and spin restrictions, there arise different  $\chi_N$  modulating factors for each one of the multiplet microstates. To illustrate this fact, we present, in what follows, the explicit expressions for the exchange-energy functional associated with particular microstates of the carbon atom multiplets.

From eq. (27), it follows that the exchange-energy functional for the  $\Psi_1(^3P)$  microstate of carbon, namely, for the wave function corresponding to the  $1s^2 2s^2 2p^2$  configuration [where  $2p^2$  has the

**TABLE III.**  
**Energy Parameters for  $^3P$ ,  $^1D$ ,  $^1S$  Terms of C Atom (in Hartrees).**

Term	Method	$-E$	$T_s$	$-E_x^a$	$-\epsilon_{2p}$
$^3P$	HF	37.68862	37.68862	5.05416	0.433
	LS-DFT <sup>b</sup>	37.68669	37.68919	5.05272	0.432
$^1D$	HF	37.63133	37.63133	4.95663	0.381
	LS-DFT <sup>b</sup>	37.62979	37.63239	4.95610	0.381
$^1S$	HF	37.54961	37.54961	4.64669	0.310
	LS-DFT <sup>b</sup>	37.54702	37.55104	4.64417	0.311

<sup>a</sup> Exchange energy expressions are different for every term [eqs. (63)–(66) for  $^3P$ , with similar equations for other terms].

<sup>b</sup> Minimization of the energy functional of eq. (17) calculated with scaled orbitals [eqs. (30)–(34)] at fixed density  $\rho = \rho_{HF}$ .

1-matrix indicated in eq. (55)] is:

$$E_x[\Phi_\rho] = -\frac{1}{2} \int_0^\infty dr_1 r_1^2 \left[ \rho(r_1)^{4/3} \times \left( \frac{1}{1 + \vec{r}_1 \cdot \nabla_r \ln \lambda(r_1)} \right)^{1/3} \chi_6^0(f_1) + \rho(r_1)^{5/3} \left( \frac{1}{1 + \vec{r}_1 \cdot \nabla_r \ln \lambda(r_1)} \right)^{2/3} \chi_6^1(f_1) + \rho(r_1)^2 \left( \frac{1}{1 + \vec{r}_1 \cdot \nabla_r \ln \lambda(r_1)} \right) \chi_6^2(f_1) \right] \quad (63)$$

where the exchange modulating factors are:

$$\chi_6^0(f_1) = \frac{1}{f_1 \rho_g^{4/3}(f_1)} \left[ 2G_{1s1s}^0(f_1) + 4G_{1s2s}^0(f_1) + 2G_{2s2s}^0(f_1) + 2G_{2p2p}^0(f_1) \right] \quad (64)$$

$$\chi_6^1(f_1) = \frac{1}{f_1^2 \rho_g^{5/3}(f_1)} \left[ \frac{4}{3} G_{1s2p}^1(f_1) + \frac{4}{3} G_{2s2p}^1(f_1) \right] \quad (65)$$

$$\chi_6^2(f_1) = \frac{1}{f_1^3 \rho_g^2(f_1)} \frac{11}{25} G_{2p2p}^2(f_1) \quad (66)$$

An expression similar to eq. (63) ensues for the  $\Psi_{10}(^1D)$  microstate. In fact, the modulating factors,  $\chi_6^0(f_1)$  and  $\chi_6^1(f_1)$ , are precisely those of eqs. (64) and (65), respectively. However,  $\chi_6^2(f_1)$  is given in this case by:

$$\chi_6^2(f_1) = \frac{1}{f_1^3 \rho_g^2(f_1)} \frac{2}{25} G_{2p2p}^2(f_1) \quad (67)$$

For the  $\Psi_{15}(^1S)$  microstate, we have the following exchange modulating factors:

$$\chi_6^0(f_1) = \frac{1}{f_1 \rho_g^{4/3}(f_1)} \left[ 2G_{1s1s}^0(f_1) + 4G_{1s2s}^0(f_1) + 2G_{2s2s}^0(f_1) + \frac{2}{3} G_{2p2p}^0(f_1) \right] \quad (68)$$

$$\chi_6^2(f_1) = \frac{1}{f_1^3 \rho_g^2(f_1)} \frac{4}{15} G_{2p2p}^2(f_1) \quad (69)$$

In this case,  $\chi_6^1(f_1)$  is the same as that of eq. (65).

In Table III, we present LS-DFT results for the multiplets of carbon. We list for comparison the corresponding Hartree–Fock values. The LS-DFT calculations are based on a density-constrained minimization of the energy functional described by eq. (17), where  $\Phi_g$  is the multiplet wave function constructed from the set of generalized Slater-type orbitals, eqs. (30)–(34) (in this case, one of the wave functions  $\{\Psi_i\}$ ). The multiplet Hartree–Fock densities were taken to be the constraining ones. Although we do not show the particular exchange energies for each one of the microstates (they have different values, which, however, when combined with the direct Coulomb term lead to the same two-electron energy expression for each multiplet), we do present the average exchange energy which, for example, for the  $^3P$  multiplet is:

$$E_x^{av}(^3P) \equiv \frac{1}{9} \sum_{i=1}^9 E_x[\Psi_i(^3P)] \\ = -G^0(1s1s) - 2G^0(1s2s) - G^0(2s2s) \\ - \frac{2}{3} G^1(1s2p) - \frac{2}{3} G^1(2s2p) \\ + G^0(2p2p) - \frac{6}{25} G^2(2p2p) \quad (70)$$

where  $G^k(ij)$  are the usual exchange integrals.<sup>60</sup> The results obtained by means of the explicit energy-density functionals advanced here lead to values in close agreement with the Hartree–Fock ones. The error in all cases studied is of the order of millihartrees. Moreover, all the energies calculated satisfy the variational principle, as they are upper bounds to the Hartree–Fock results. In particular, the value of the  $\epsilon_{2p}$  orbital energy is in excellent agreement with the corresponding Hartree–Fock value.

In Table IV, we present results of density-constrained kinetic energy minimizations for these multiplets, namely, Kohn–Sham exchange-only values for single-particle energies, kinetic, exchange, and total energies. In addition, we include values for  $\int v^{KS} \rho dv$  and  $\sum_i \epsilon_i - T$ . For comparison we have also listed Hartree–Fock as well as values recently reported by Nagy.<sup>77</sup> The local-scaling transformation results have been obtained by using both generalized Slater-type orbitals and even-

tempered orbital expansions (with eight functions for  $s$ - and six functions for  $p$ -orbitals). We observe, in the first place, that, although the kinetic energies obtained from the even-tempered orbital expansion show improvements of the order of millihartrees with respect to those based on generalized Slater-type orbitals, they are still higher than those presented by Nagy<sup>77</sup> (Rydbergs are used in this table for ease of comparison with Nagy’s results). But, in view of the fact that the even-tempered orbital basis is flexible enough, our results should closely approach the extremum of the kinetic energy minimization problem as we make no approximation other than the choice of a limited orbital expansion. Second, we see that there is a fair agreement between  $\int v^{KS} \rho dv$  and  $\sum_i \epsilon_i - T$  for each one the methods used, although they differ from method to method. Third, as expected, we observe that the orbital eigenvalues are very sensitive to the procedure employed. Finally, we may also conclude from Table IV that there is an excel-

**TABLE IV.**  
**Kohn–Sham x-Only Energy Characteristics for Multiplets of C Atom (in Rydbergs).**

Term	Value	LST-DFT <sup>a</sup>	LST-DFT <sup>b</sup>	Ref. 77	HF <sup>c</sup>
<sup>3</sup> P	$-\epsilon_{1s}$	20.766	20.706	20.707	22.651
	$-\epsilon_{2s}$	1.497	1.498	1.505	1.411
	$-\epsilon_{2p}$	0.860	0.860	0.867	0.867
	$T$	75.3756	75.3732	75.372	75.3772
	$E$	−75.3706	−75.3736	−75.372	−75.3772
	$E_x^d$	−10.0233	−10.0239		−10.0305
	$\int v^{KS} \rho dv$	−121.6204	−121.4996		
	$\sum_i \epsilon_i - T$	−121.6230	−121.4997	−121.530	
<sup>1</sup> D	$-\epsilon_{1s}$	20.698	20.622	20.607	22.703
	$-\epsilon_{2s}$	1.400	1.396	1.398	1.437
	$-\epsilon_{2p}$	0.766	0.761	0.763	0.763
	$T$	75.2628	75.2602	75.259	75.2627
	$E$	−75.2575	−75.2606	−75.258	−75.2627
	$E_x^d$	−9.9883	−9.9886		−9.9935
	$\int v^{KS} \rho dv$	−120.9901	−120.8187		
	$\sum_i \epsilon_i - T$	−120.9929	−120.8188	−120.795	
<sup>1</sup> S	$-\epsilon_{1s}$	20.610	20.503	20.481	22.783
	$-\epsilon_{2s}$	1.268	1.252	1.252	1.479
	$-\epsilon_{2p}$	0.639	0.623	0.623	0.620
	$T$	75.1000	75.0966	75.099	75.0992
	$E$	−75.0919	−75.0970	−75.094	−75.0992
	$E_x^d$	−9.9325	−9.9321		−9.9349
	$\int v^{KS} \rho dv$	−120.1318	−119.8523		
	$\sum_i \epsilon_i - T$	−120.1355	−119.8523	−119.811	

<sup>a</sup> Minimization of kinetic energy calculated with scaled orbitals eqs. (30)–(34) at fixed density  $\rho = \rho_{HF}$ . <sup>b</sup> Minimization of kinetic energy calculated with scaled even-tempered orbitals (eight-term for  $s$ - and six-term for  $p$ -orbitals) at fixed density  $\rho = \rho_{HF}$ . <sup>c</sup> HF values obtained by numerical program of Froese-Fischer.<sup>62</sup> <sup>d</sup> Calculated with spherical averaging (see footnote in Table II).

lent agreement (with differences in milli-Rydbergs) between our present results and those recently reported by Nagy.<sup>77</sup>

## Correlation Energy Decomposition

A rigorous procedure for accomplishing a decomposition of the correlation energy into its dynamical and nondynamical components has been recently put forward in the context of LS-DFT.<sup>49</sup> We briefly comment here on some of the main aspects of this decomposition for the purpose of indicating how it is possible to define a reference wave function that differs from the exact one in just the dynamical part of electron correlation. Then, we use this reference wave function to separate the calculation of the correlation energy into two parts:  $E_c(\Psi^{HF} \rightarrow \Psi^R)$  and  $E_c(\Psi^R \rightarrow \Psi^{exact})$  [see eq. (75) later]. We claim that these two components are related to “long-range” and “short-range” correlation, respectively, and that, due to their essentially different nature, they can be treated by entirely different methods.

Correlation energy is defined by Löwdin<sup>79</sup> as the difference between the exact nonrelativistic and the restricted Hartree–Fock energies:

$$E_c \equiv E_0^{exact} - E_0^{HF} = \mathcal{E}[\rho_{exact}, \Psi^{exact}] - \mathcal{E}[\rho_{HF}, \Psi^{HF}] \quad (71)$$

Note that, as shown in the right-hand side of eq. (71), the correlation energy can also be written as the difference of energy functionals of the type given by eq. (16). In fact, when we add and subtract the functional  $\mathcal{E}[\rho_{HF}, \Psi^{exact}]$  (which represents the expectation value with respect to  $\hat{H}$  of the wave function,  $\Psi_{\rho_{HF}}^{exact}$ , namely, of a locally scaled exact wave function that yields the Hartree–Fock density) we obtain:

$$E_c = (\mathcal{E}[\rho_{exact}, \Psi^{exact}] - \mathcal{E}[\rho_{HF}, \Psi^{exact}]) + (\mathcal{E}[\rho_{HF}, \Psi^{exact}] - \mathcal{E}[\rho_{HF}, \Psi^{HF}]) = E_c(ndI) + E_c(dI) \quad (72)$$

where  $E_c(ndI)$  and  $E_c(dI)$  label the nondynamical and dynamical components of the correlation energy along a path that we denote as  $I$ . A locally scaled exact wave function that yields the Hartree–Fock density can be generated *in practice* by

applying local-scaling transformations connecting the exact and the Hartree–Fock densities, to each one of the coordinates of the “exact” wave function (for a particular system). The transformed wave function is given by:

$$\Psi_{\rho_{HF}}^{exact}(\vec{r}_1, s_1, \dots, \vec{r}_N, s_N) \equiv \prod_{i=1}^N \sqrt{\frac{\rho_{HF}(\vec{r}_i)}{\rho_{exact}(\vec{f}(\vec{r}_i))}} \times \Psi_{\rho_{exact}}(\vec{f}(\vec{r}_1), s_1, \dots, \vec{f}(\vec{r}_N), s_N) \quad (73)$$

where  $\vec{f}(\vec{r}) = \lambda(\vec{r})\vec{r}$  is the locally scaled vector satisfying eq. (1). In the actual applications described in what follows, “exact” wave functions correspond either to highly accurate CI expansions or MCSCF wave functions. A similar decomposition along a different path (which we label path II) is obtained by adding and subtracting  $\mathcal{E}[\rho_{exact}, \Psi^{HF}]$  from eq. (72):

$$E_c = (\mathcal{E}[\rho_{exact}, \Psi^{exact}] - \mathcal{E}[\rho_{exact}, \Psi^{HF}]) + (\mathcal{E}[\rho_{exact}, \Psi^{HF}] - \mathcal{E}[\rho_{HF}, \Psi^{HF}]) = E_c(dII) + E_c(ndII) \quad (74)$$

The interpretation of the decomposition described by eq. (72) is as follows: the nondynamical component,  $E_c(ndI)$ , represents the change in correlation energy arising from the transformation of the exact wave function locally scaled to give  $\rho_{HF}$  to the exact wave function proper. Notice that there is no change in the “form” of the wave function, but just in the type of density with which the wave function associates. On the other hand, the dynamical component,  $E_c(dI)$ , stems from the change in the “form” of the wave function (it goes from  $\Psi^{HF}$  to  $\Psi^{exact}$ , although the latter is constrained to associate with the Hartree–Fock density). Thus, in a way, the dynamical correlation along path  $I$  corresponds to the formation of the Coulomb hole (at fixed Hartree–Fock density).

Now, let us consider an intermediate reference wave function,  $\Psi^R$ , lying somewhere between the Hartree–Fock wave function and the exact one. For example, when there are near-degeneracies about the Hartree–Fock level, then a reference wave function can be constructed such that it incorporates these near-lying states. In this case,

the Löwdin correlation energy can be decomposed as follows:

$$\begin{aligned} E_c &= (\mathcal{E}[\rho_R, \Psi^R] - \mathcal{E}[\rho_{HF}, \Psi^{HF}]) \\ &\quad + (\mathcal{E}[\rho_{exact}, \Psi^{exact}] - \mathcal{E}[\rho_R, \Psi^R]) \\ &= E_c(\Psi^{HF} \rightarrow \Psi^R) + E_c(\Psi^R \rightarrow \Psi^{exact}) \quad (75) \end{aligned}$$

We assume that  $\Psi^R$  is a variational wave function whose energy expectation value is located below the Hartree–Fock energy and above the exact one. It is possible, as we did above, to decompose  $E_c(\Psi^R \rightarrow \Psi^{exact})$  into its dynamical and nondynamical components along paths  $I'$  and  $II'$ :

$$\begin{aligned} E_c(\Psi^R \rightarrow \Psi^{exact}) &= (\mathcal{E}[\rho_{exact}, \Psi^{exact}] - \mathcal{E}[\rho_R, \Psi^{exact}]) \\ &\quad + (\mathcal{E}[\rho_R, \Psi^{exact}] - \mathcal{E}[\rho_R, \Psi^R]) \\ &= E_c(\Psi^R \rightarrow \Psi^{exact}, ndI') \\ &\quad + E_c(\Psi^R \rightarrow \Psi^{exact}, dI') \quad (76) \end{aligned}$$

and:

$$\begin{aligned} E_c(\Psi^R \rightarrow \Psi^{exact}) &= (\mathcal{E}[\rho_{exact}, \Psi^{exact}] - \mathcal{E}[\rho_{exact}, \Psi^R]) \\ &\quad + (\mathcal{E}[\rho_{exact}, \Psi^R] - \mathcal{E}[\rho_R, \Psi^R]) \\ &= E_c(\Psi^R \rightarrow \Psi^{exact}, dII') \\ &\quad + E_c(\Psi^R \rightarrow \Psi^{exact}, ndII') \quad (77) \end{aligned}$$

From the variational character of  $\Psi^R$ , it follows that  $E_c(\Psi^R \rightarrow \Psi^{exact}, ndII') \geq 0$  and also that  $E_c(\Psi^R \rightarrow \Psi^{exact}, ndI') \leq 0$ , allowing the possibility of finding a reference wave function for which, in both cases, the equal sign holds, or at least for which these quantities approach zero as closely as possible. To see what is at stake when this condition is satisfied, let us look in detail at the nature of the nondynamical correlation term:

$$\begin{aligned} E_c(\Psi^R \rightarrow \Psi^{exact}, ndII') &= (\mathcal{E}[\rho_{exact}, \Psi^R] - \mathcal{E}[\rho_R, \Psi^R]) \\ &= (T[\rho_{exact}, \Psi^R] - T[\rho_R, \Psi^R]) \\ &\quad + \frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \end{aligned}$$

$$\begin{aligned} &\times \frac{(\rho_{exact}(\vec{r}_1)\rho_{exact}(\vec{r}_2) - \rho_R(\vec{r}_1)\rho_R(\vec{r}_2))}{|\vec{r}_1 - \vec{r}_2|} \\ &+ \int d^3\vec{r} [\rho_{exact}(\vec{r}) - \rho_R(\vec{r})] v(\vec{r}) \\ &+ (E_{xc}[\rho_{exact}, \Psi_R] - E_{xc}[\rho_R, \Psi_R]) \quad (78) \end{aligned}$$

It is clear that the magnitude of this difference depends upon the proximity between  $\rho_R$  and  $\rho_{exact}$  (when both are equal, it is identically zero).

To define rigorously the reference wave function,  $\Psi^R$ , let us consider a finite set of one-particle orbitals,  $\{\phi_i\}_{i=1}^m$ , where  $m > N$ , from which we construct a finite set of Slater determinants,  $\{\Phi_I\}$ . These, in turn can be used to construct a set of configuration state functions,  $\{\Psi_I^{CSF}\}$ , satisfying the angular momentum and spin symmetry requirements of the system under consideration. Then, the reference wave function is expanded over this set:

$$\Psi^R = \sum_I C_I \Psi_I^{CSF} \quad (79)$$

and the coefficients of this expansion are determined so as to minimize the total energy subject to the constraint that point by point:

$$\rho_R(\vec{r}) = \rho_{exact}(\vec{r}) \quad (80)$$

(Similar variational problems have been considered earlier by Nguyen-Dang et al.<sup>80</sup> and by Zhao et al.<sup>81</sup>). In eq. (79) the configuration state functions are linear combinations of Slater determinants:

$$\Psi_I^{CSF} = \sum_K a_K \Phi_K \quad (81)$$

where the expansion coefficients,  $a_K$ , are fixed by the operators  $\hat{L}^2$  and  $\hat{L}_Z$  and  $\hat{S}^2$  and  $\hat{S}_Z$ , and where  $\Phi_K$  is the Slater determinant:

$$\Phi_K(\vec{r}_1, \dots, \vec{r}_N) = \frac{\det}{\sqrt{N!}} \{ \phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N) \} \quad (82)$$

In analogy with eq. (76), one may decompose  $E_c(\Psi^{HF} \rightarrow \Psi^R)$  into its dynamical and nondynamical components:

$$\begin{aligned} E_c(\Psi^{HF} \rightarrow \Psi^R) &= (\mathcal{E}[\rho_R, \Psi^R] - \mathcal{E}[\rho_{HF}, \Psi^R]) \\ &\quad + (\mathcal{E}[\rho_{HF}, \Psi^R] - \mathcal{E}[\rho_{HF}, \Psi^{HF}]) \\ &= E_c(\Psi^{HF} \rightarrow \Psi^R, ndI') \\ &\quad + E_c(\Psi^{HF} \rightarrow \Psi^R, dI') \quad (83) \end{aligned}$$

The values for the dynamical and nondynamical components of both  $E_c(\Psi^{HF} \rightarrow \Psi^R)$  and  $E_c(\Psi^R \rightarrow \Psi^{exact})$  for several approximate reference wave functions for the Be isoelectronic series are presented in Table V. As reference wave functions for the beryllium atom and members of its isoelectronic series we have used the limited configuration interaction wave functions described in Table V. As it can be seen in this table, the dynamical components are by far the dominant ones in both  $E_c(\Psi^{HF} \rightarrow \Psi^R)$  and  $E_c(\Psi^R \rightarrow \Psi^{exact})$ . However, the ratio of nondynamical to dynamical components in the former is of the order of  $10^{-1}$ , whereas in the latter it is of  $10^{-3}$ . But beyond this comparison, we observe, in this table, that a remarkable

gain in correlation energy takes place by the mere addition of the  $(2p^2, ^1S)$  configuration to the Hartree-Fock wave function. This gain is comparable to the whole improvement corresponding to  $E_c(\Psi^R \rightarrow \Psi^{exact})$ . By adding other low-lying configurations one gets only a very slight improvement. Hence, it seems that the two components,  $E_c(\Psi^{HF} \rightarrow \Psi^R)$  and  $E_c(\Psi^R \rightarrow \Psi^{exact})$ , are of a different nature and that, consequently, they should be treated by different density functional methods.

The fact that such a large correlation energy improvement is obtained for  $E_c(\Psi^{HF} \rightarrow \Psi^R)$  through the addition of configurations that have a manifest influence on the density (a global quantity for the system) shows that this part of the

**TABLE V.**  
**Components of Correlation Energy ( $\mu$ hartrees) Obtained by Decomposition of Reference Wave Functions for Be Isoelectronic Series.<sup>a</sup>**

		$\Psi_I^R$	$\Psi_{II}^R$	$\Psi_{III}^R$	$\Psi_{IV}^R$
Be	$E_c(\Psi^{HF} \rightarrow \Psi^R)$	-43,822	-45,388	-43,953	-44,250
	$E_c(dl)$	-41,660	-43,309	-41,830	-42,163
	$E_c(ndl)$	-2,162	-2,079	-2,123	-2,087
	$E_c(\Psi^R \rightarrow \Psi_\rho)$	-47,450	-45,884	-47,319	-47,022
	$E_c(dl')$	-47,393	-45,852	-47,261	-46,953
	$E_c(ndl')$	-57	-32	-58	-69
	$E_c(\Psi^{HF} \rightarrow \Psi_\rho) =$	-91,272			
B <sup>+</sup>	$E_c(\Psi^{HF} \rightarrow \Psi^R)$	-58,803	-60,236	-58,941	-59,495
	$E_c(dl)$	-54,802	-56,284	-54,992	-55,714
	$E_c(ndl)$	-4,001	-3,952	-3,949	-3,781
	$E_c(\Psi^R \rightarrow \Psi_\rho)$	-48,973	-47,540	-48,835	-48,281
	$E_c(dl')$	-48,953	-47,526	-48,814	-48,254
	$E_c(ndl')$	-20	-14	-21	-27
	$E_c(\Psi^{HF} \rightarrow \Psi_\rho) =$	-107,776			
C <sup>2+</sup>	$E_c(\Psi^{HF} \rightarrow \Psi^R)$	-72,461	-73,860	-72,604	-73,346
	$E_c(dl)$	-65,655	-67,115	-65,861	-66,925
	$E_c(ndl)$	-6,806	-6,745	-6,743	-6,421
	$E_c(\Psi^R \rightarrow \Psi_\rho)$	-49,278	-47,879	-49,135	-48,393
	$E_c(dl')$	-49,263	-47,864	-49,120	-48,376
	$E_c(ndl')$	-15	-15	-15	-17
	$E_c(\Psi^{HF} \rightarrow \Psi_\rho) =$	-121,739			
N <sup>3+</sup>	$E_c(\Psi^{HF} \rightarrow \Psi^R)$	-85,489	-86,881	-85,635	-86,518
	$E_c(dl)$	-74,971	-76,454	-75,194	-76,566
	$E_c(ndl)$	-10,518	-10,427	-10,441	-9,952
	$E_c(\Psi^R \rightarrow \Psi_\rho)$	-49,460	-48,077	-49,324	-48,446
	$E_c(dl')$	-49,451	-48,068	-49,314	-48,431
	$E_c(ndl')$	-9	-9	-10	-15
	$E_c(\Psi^{HF} \rightarrow \Psi_\rho) =$	-134,946			

$\Psi_I^R = (1s^2, ^1S)[C_1(2s^2, ^1S) + C_2(2p^2, ^1S)]^1S$ ;  $\Psi_{II}^R = (1s^2, ^1S)[C_1(2s^2, ^1S) + C_2(2p^2, ^1S) + C_3(3s^2, ^1S)]^1S$ ;  $\Psi_{III}^R = (1s^2, ^1S)[C_1(2s^2, ^1S) + C_2(2p^2, ^1S) + C_3(3p^2, ^1S)]^1S$ ;  $\Psi_{IV}^R = (1s^2, ^1S)[C_1(2s^2, ^1S) + C_2(2p^2, ^1S) + C_3(3d^2, ^1S)]^1S$ .

<sup>a</sup>  $\Psi_\rho$  is a 140-CSF MCSCF wave function.



correlation energy has a long-range character. The effect on one-particle density is examined in Figure 4 where we plot the difference between the densities,  $\rho_R$  (coming from the approximate reference wave functions  $\Psi_I^R$  and  $\Psi_{II}^R$ ), and both  $\rho_{HF}$  and  $\rho$  (the latter arising from a 140-term MCSCF wave function<sup>82</sup>). For comparison, the difference between  $\rho_{HF}$  and  $\rho$  is also given. As expected,  $\rho_R$  in all cases examined differs greatly from  $\rho_{HF}$  and approaches quite closely the exact density  $\rho_{exact}$ .

In marked contrast with what happens with  $E_c(\Psi^{HF} \rightarrow \Psi^R)$ , we observe that  $E_c(\Psi^R \rightarrow \Psi^{exact})$  can only be improved through the use of very large configuration interaction expansions, which do not show much effect on the one-particle density. One may conclude, therefore, that  $E_c(\Psi^R \rightarrow \Psi^{exact})$  is due chiefly to short-range interactions.

Because, according to eq. (75) the “long-range” part of the correlation energy is defined by  $E_c(\Psi^{HF} \rightarrow \Psi^R) = \mathcal{E}[\rho_R, \Psi^R] - \mathcal{E}[\rho_{HF}, \Psi^{HF}]$ , it follows that local-scaling transformations can be used for the purpose of constructing an explicit density functional expression. For the functional  $\mathcal{E}[\rho_R, \Psi^R]$  this would involve just the inclusion of some small modifications on the method already applied to  $\mathcal{E}[\rho_{HF}, \Psi^{HF}]$  in the second section. Let us remark that, in this case,  $E_c(\Psi^{HF} \rightarrow \Psi^R, dI')$  is the dynamical contribution to the “long-range” correlation energy.

We claim, on the other hand, that the calculation of the “short-range” component  $E_c(\Psi^R \rightarrow \Psi^{exact}, dI')$  requires that we include, in some ade-

quate way, the local Coulomb hole. We propose that this can be accomplished by means of an explicit use of a correlation factor. The problem of how to deal with  $E_c(\Psi^R \rightarrow \Psi^{exact}, dI')$  in the context of LS-DFT is treated in the following section.

## Cluster Expansion Procedure for “Short-Range” Dynamical Correlation

In a previous article,<sup>83</sup> we have considered the treatment of electron correlation in terms of a cluster expansion based on a single Slater determinant. In this section, we extend these ideas to deal with dynamical “short-range” correlation, where, instead of a determinant, we have a multireference wave function,  $\Psi^R$ .

Consider the following approximation to the exact wave function:

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = C(\vec{r}_1, \dots, \vec{r}_N) \Psi^R(\vec{r}_1, \dots, \vec{r}_N) \quad (84)$$

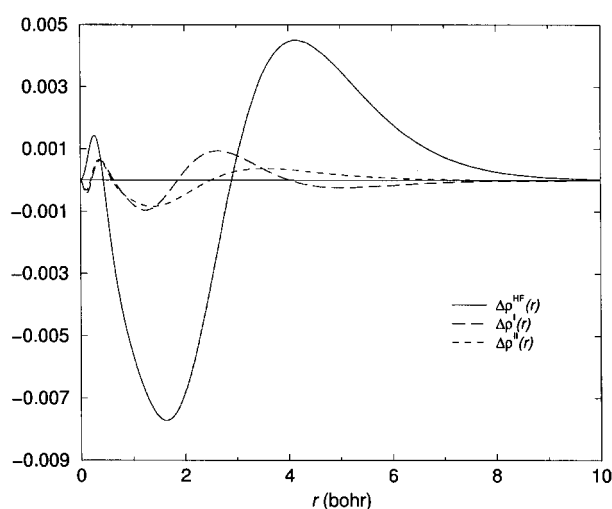
where the  $N$ -particle correlation function  $C$  is the product of two-particle correlation functions  $g(\vec{r}_i, \vec{r}_j)$ :

$$C(\vec{r}_1, \dots, \vec{r}_N) = \prod_{i>j} g(\vec{r}_i, \vec{r}_j) \quad (85)$$

and where  $\Psi^R$  is defined as the linear combination of configuration-state functions described by eq. (79). We assume that the  $\Psi_I^{CSF}$  values are constructed from a simple set, such as the generalized Slater-type orbitals described by eqs. (30)–(34). Clearly, because these orbitals are at best approximations of the Kohn–Sham orbitals, we cannot expect  $\Psi^R$  to yield the exact density. Hence, the approximate wave function given by eq. (84) can be improved through the application of density transformations. The density-transformed wave function therefore becomes:

$$\Psi_\rho(\vec{r}_1, \dots, \vec{r}_N) = C(\vec{f}_1, \dots, \vec{f}_N) \tilde{\Psi}^R(\vec{r}_1, \dots, \vec{r}_N) \quad (86)$$

where  $\tilde{\Psi}^R$  is the density-transformed reference wave function defined by eqs. (79) and (81), but where in the transformed Slater determinants [eq. (82)] each one of the initial orbitals has been locally



**FIGURE 4.** Density differences for the Hartree–Fock and some reference states with respect to the “exact” density.

transformed. Thus, eq. (82) becomes:

$$\tilde{\Phi}_K(\vec{r}_1, \dots, \vec{r}_N) = \frac{\det}{\sqrt{N!}} \left\{ \sqrt{\frac{\rho(\vec{r}_1)}{\rho_\Psi(\vec{f}_1)}} \phi_{K_1}(\vec{f}_1), \dots, \sqrt{\frac{\rho(\vec{r}_N)}{\rho_\Psi(\vec{f}_N)}} \phi_{K_N}(\vec{f}_N) \right\} \quad (87)$$

As it has been shown elsewhere,<sup>83</sup> the energy expression takes the form:

$$E[\Psi_\rho] \equiv \frac{\langle \tilde{\Psi}^R | \prod_{i>j}^N g^2(\vec{f}_i, \vec{f}_j) \left[ \hat{H} + \sum_{i<j} \hat{u}(\vec{f}_i, \vec{f}_j) + \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq i,j}^N \hat{F}_{ijk} \right] | \tilde{\Psi}^R \rangle}{\langle \tilde{\Psi}^R | \prod_{i>j}^N g^2(\vec{f}_i, \vec{f}_j) | \tilde{\Psi}^R \rangle} \geq E_0 \quad (88)$$

where:

$$\hat{u}(\vec{f}_i, \vec{f}_j) = -\frac{1}{2} \frac{(\nabla_{\vec{r}_i}^2 + \nabla_{\vec{r}_j}^2) g(\vec{f}_i, \vec{f}_j)}{g(\vec{f}_i, \vec{f}_j)} - \frac{\nabla_{\vec{r}_i} g(\vec{f}_i, \vec{f}_j) \cdot \nabla_{\vec{r}_i} + \nabla_{\vec{r}_j} g(\vec{f}_i, \vec{f}_j) \cdot \nabla_{\vec{r}_j}}{g(\vec{f}_i, \vec{f}_j)} \quad (89)$$

and:

$$\hat{F}_{ijk} = -\frac{1}{2} \frac{\nabla_{\vec{r}_i}^2 g(\vec{f}_i, \vec{f}_j)}{g(\vec{f}_i, \vec{f}_j)} - \frac{\nabla_{\vec{r}_i} g(\vec{f}_i, \vec{f}_j) \cdot \nabla_{\vec{r}_i} g(\vec{f}_i, \vec{f}_k)}{g(\vec{f}_i, \vec{f}_j) g(\vec{f}_i, \vec{f}_k)} \quad (90)$$

By resorting to the Aviles–Hartog–Tolhoek cluster expansion<sup>84,85</sup> we can rewrite the energy as:

$$E[\Psi_\rho] = \frac{1}{\langle \Psi_\rho | \Psi_\rho \rangle} \frac{\partial I_N(\beta)}{\partial \beta} \bigg|_{\beta=0} = \sum_{k=1}^N E^{(k)}[\Psi_\rho] \quad (91)$$

where  $I_N(\beta)$  is the cluster subintegral:

$$I_n(\beta) = \langle \tilde{\Phi} | \prod_{i>j}^n g(\vec{f}_i, \vec{f}_j) e^{\beta \hat{H}_n} \prod_{i>j}^n g(\vec{f}_i, \vec{f}_j) | \tilde{\Phi} \rangle \quad (92)$$

and where the cluster energy contributions,  $E^{(k)}[\Psi_\rho]$ , are<sup>86</sup>:

$$E^{(k)}[\Psi_\rho] = C_{n,k} \frac{\partial \ln \mathcal{Z}_k(\beta)}{\partial \beta} \bigg|_{\beta=0} \quad (93)$$

The cluster functions  $\{\mathcal{Z}_k(\beta)\}$  are defined through:

$$I_n(\beta) = \prod_{k=1}^n \mathcal{Z}_k^{C_{n,k}}(\beta) \quad (94)$$

where  $C_{n,k} = n!/(n-k)!k!$ . In the FAHT cluster expansion we can approximate  $I_n$  of eq. (94) by assuming that the cluster functions,  $\{\mathcal{Z}_k(\beta)\}$ , are equal to 1 after a given value of  $k \leq N$ . Hence, for a second-order cluster expansion (which is obtained by requiring that  $\mathcal{Z}_k(\beta) = 1$  for  $k = 3, \dots, N$ ) the energy is approximated by:

$$E[\Psi_\rho] \simeq E^{(1)}[\Psi_\rho] + E^{(2)}[\Psi_\rho] \quad (95)$$

By subtracting from this expression  $E[\tilde{\Psi}^R]$  we obtain the following approximate expression for the dynamical “short-range” correlation:

$$\begin{aligned} E_c(\Psi^R \rightarrow \Psi_\rho, d) & \simeq E_c^{(1)}[\Psi_\rho] + E_c^{(2)}[\Psi_\rho] - E[\hat{\Psi}^R] \\ & = \frac{\langle \tilde{\Psi}^R | \sum_{i<j}^N (1 + \phi(\vec{f}_i, \vec{f}_j)) \hat{u}_{ij} | \tilde{\Psi}^R \rangle}{\langle \tilde{\Psi}^R | \tilde{\Psi}^R \rangle + \langle \tilde{\Psi}^R | \phi(\vec{f}_1, \vec{f}_2) | \tilde{\Psi}^R \rangle} \\ & \quad + \frac{\langle \tilde{\Psi}^R | \sum_{i<j}^N \hat{h}_{ij} | \tilde{\Psi}^R \rangle}{\langle \tilde{\Psi}^R | \tilde{\Psi}^R \rangle} \\ & \quad \times \sum_{k=1}^{\infty} (-1)^k \left( \frac{\langle \tilde{\Psi}^R | \phi(\vec{f}_1, \vec{f}_2) | \tilde{\Psi}^R \rangle}{\langle \tilde{\Psi}^R | \tilde{\Psi}^R \rangle} \right)^k \\ & \quad + \frac{\langle \tilde{\Psi}^R | \sum_{i<j}^N \phi(\vec{f}_i, \vec{f}_j) \hat{h}_{ij} | \tilde{\Psi}^R \rangle}{\langle \tilde{\Psi}^R | \tilde{\Psi}^R \rangle + \langle \tilde{\Psi}^R | \phi_{12} | \tilde{\Psi}^R \rangle} \end{aligned} \quad (96)$$

where  $\phi_{ij}$  is given by  $g^2(\vec{f}_i, \vec{f}_j) = 1 + \phi(\vec{f}_i, \vec{f}_j)$ , and where the two-particle operator is:

$$\hat{h}_{ij} = \hat{F}_i + \hat{F}_j + v_{ij} \quad (97)$$

with  $v_{ij} = 1/|\vec{r}_i - \vec{r}_j|$  and  $\hat{F}_i = (1/2) \nabla_{\vec{r}_i}^2 - Z/r_i$ . It is clear that, through the presence of the transformed vector,  $\vec{f}_i = \vec{f}_i[\rho; \vec{r}]$  in  $\phi(\vec{f}_i, \vec{f}_j)$ , and also

in the wave function,  $\Psi^R$  [see eq. (87)], the whole expression in eq. (96) is an implicit functional of the one-particle density,  $\rho$ . Clearly, eq. (96) can be transformed into an explicit functional of  $\rho$  by using the procedure advanced in ref. 83.

## Generation of Density Transformations for Diatomic Molecules

### GENERAL TREATMENT

In the general procedure for determining a density transformation advanced by Moser<sup>87</sup> and, more recently, by Bokanowski and Gréber<sup>53</sup> one considers two volume elements,  $\tau = g(\vec{r}) d^3\vec{r}$  and  $\sigma = h(\vec{r}) d^3\vec{r}$ , in the unit cube  $Q \equiv [0, 1]^3$ . If  $\int_Q g(\vec{r}) d^3\vec{r} = \int_Q h(\vec{r}) d^3\vec{r}$ , then there exists a transformation,  $\vec{R}_\rho = \vec{R}_\rho(\vec{r})$ , such that  $g(\vec{R}_\rho(\vec{r})) d^3\vec{R}_\rho = h(\vec{r}) d^3\vec{r}$ .

Given a wave function formed by plane waves, whose density is  $\rho_0 = N$  in the unit cube, and then applying the coordinate-transformation operator,  $\hat{R}_{\rho_1}$ , to each one of the coordinates of this wave function, we can generate a transformed wave function containing density-scaled plane waves that associates with the density,  $\rho_1(\vec{r})$ . This density is connected to the initial one through:

$$\rho_1(\vec{r}) = J(\vec{R}_{\rho_1}; \vec{r}) \rho_0(\vec{R}_{\rho_1}) \quad (98)$$

where  $J(\vec{R}_{\rho_1}; \vec{r})$  is the Jacobian. Similarly, for a density  $\rho_2(\vec{r})$  we have:

$$\rho_2(\vec{r}) = J(\vec{R}_{\rho_2}; \vec{r}) \rho_0(\vec{R}_{\rho_2}) \quad (99)$$

The general density transformation from  $\rho_1$  to  $\rho_2$  satisfies the equation:

$$\rho_2(\vec{r}) = J(\vec{f}; \vec{r}) \rho_1(\vec{f}) \quad (100)$$

If we denote the operators for the transformations given in eqs. (98), (99), and (100) by  $\hat{R}_{\rho_1}$ ,  $\hat{R}_{\rho_2}$ , and  $\hat{f}$ , respectively, we observe that they are related through:

$$\hat{f} = (\hat{R}_{\rho_1})^{-1} \hat{R}_{\rho_2} \quad (101)$$

or, equivalently, by:

$$\hat{R}_{\rho_1} \hat{of} = \hat{R}_{\rho_2} \quad (102)$$

where  $(\hat{R}_{\rho_1})^{-1}$  denotes the inverse transformation. We now introduce the decomposition of the above

vectors in terms of their components in prolate spheroidal coordinates:

$$\begin{aligned} \vec{r} &= (r_\lambda, r_\mu, r_\varphi) \\ \vec{f} &= (f_\lambda, f_\mu, f_\varphi) \\ \vec{R}_{\rho_1} &= (R_{1\lambda}, R_{1\mu}, R_{1\varphi}) \\ \vec{R}_{\rho_2} &= (R_{2\lambda}, R_{2\mu}, R_{2\varphi}) \end{aligned} \quad (103)$$

These coordinates are defined by the relations:

$$\begin{aligned} x &= \frac{R}{2} ((\lambda^2 - 1)(1 - \mu^2))^{1/2} \cos \varphi \\ y &= \frac{R}{2} ((\lambda^2 - 1)(1 - \mu^2))^{1/2} \sin \varphi \\ z &= \frac{R}{2} \lambda \mu \end{aligned} \quad (104)$$

From the right-hand side of eq. (102) it follows that:

$$\begin{aligned} \hat{R}_{\rho_2} o(r_\lambda, r_\mu, r_\varphi) &= (R_{2\lambda}(r_\lambda, r_\mu, r_\varphi), \\ &R_{2\mu}(r_\lambda, r_\mu, r_\varphi), R_{2\varphi}(r_\lambda, r_\mu, r_\varphi)) \\ &= (\tilde{R}_{2\lambda}(\lambda, \mu, \varphi), \tilde{R}_{2\mu}(\lambda, \mu, \varphi), \tilde{R}_{2\varphi}(\lambda, \mu, \varphi)) \end{aligned} \quad (105)$$

where, following the procedure of Zumbach and Maschke,<sup>12</sup> we have defined:

$$\begin{aligned} \tilde{R}_{2\lambda}(\lambda, \mu, \varphi) &= \frac{\int_{-1}^{\mu} \rho_2(\lambda, \mu, \varphi) (\lambda^2 - \mu^2) d\mu}{\int_{-1}^1 \rho_2(\lambda, \mu, \varphi) (\lambda^2 - \mu^2) d\mu} \\ \tilde{R}_{2\mu}(\lambda, \mu, \varphi) &= \frac{\int_1^{\lambda} \int_{-1}^1 \rho_2(\lambda, \mu, \varphi) (\lambda^2 - \mu^2) d\mu d\lambda}{\int_1^{\infty} \int_{-1}^1 \rho_2(\lambda, \mu, \varphi) (\lambda^2 - \mu^2) d\mu d\lambda} \\ \tilde{R}_{2\varphi}(\lambda, \mu, \varphi) &= \frac{\int_0^{\varphi} \int_1^{\infty} \int_{-1}^1 \rho_2(\lambda, \mu, \varphi) (\lambda^2 - \mu^2) d\mu d\lambda d\varphi}{\int_0^{2\pi} \int_1^{\infty} \int_{-1}^1 \rho_2(\lambda, \mu, \varphi) (\lambda^2 - \mu^2) d\mu d\lambda d\varphi} \end{aligned} \quad (106)$$

Similarly, from the left-hand side of eq. (102) it follows that:

$$\begin{aligned} \hat{R}_{\rho_1} \hat{of} o(r_\lambda, r_\mu, r_\varphi) &= \hat{R}_{\rho_1} o((f_\lambda(\lambda, \mu, \varphi), f_\mu(\lambda, \mu, \varphi), f_\varphi(\lambda, \mu, \varphi))) \\ &= (R_{1\lambda}(f_\lambda, f_\mu, f_\varphi), \\ &R_{1\mu}(f_\lambda, f_\mu, f_\varphi), R_{1\varphi}(f_\lambda, f_\mu, f_\varphi)) \end{aligned}$$

$$= \left( \tilde{R}_{1\lambda}(\lambda_T, \mu_T, \varphi_T), \right. \\ \left. \tilde{R}_{1\mu}(\lambda_T, \mu_T, \varphi_T), \tilde{R}_{2\varphi}(\lambda_T, \mu_T, \varphi_T) \right) \quad (107)$$

In eq. (107), the transformed prolate spheroidal coordinates are related to the Cartesian components of the vector  $\vec{f} = (f_x, f_y, f_z)$  as follows:

$$f_x = \frac{R}{2} ((\lambda_T^2 - 1)(1 - \mu_T^2))^{1/2} \cos \varphi_T \\ f_y = \frac{R}{2} ((\lambda_T^2 - 1)(1 - \mu_T^2))^{1/2} \sin \varphi_T \quad (108) \\ f_z = \frac{R}{2} \lambda_T \mu_T$$

and the components of the transformed vector are given by:

$$\tilde{R}_{1\lambda}(\lambda_T, \mu_T, \varphi_T) \\ = \frac{\int_{-1}^{\mu_T} \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T}{\int_{-1}^1 \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T} \\ \tilde{R}_{1\mu}(\lambda_T, \mu_T, \varphi_T) \\ = \frac{\int_1^{\lambda_T} \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\lambda_T}{\int_1^\infty \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\lambda_T} \\ \tilde{R}_{2\varphi}(\lambda_T, \mu_T, \varphi_T) \\ = \frac{\int_0^{\varphi_T} \int_1^1 \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T d\lambda_T d\varphi_T}{\int_0^{2\pi} \int_1^1 \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T d\lambda_T d\varphi_T} \quad (109)$$

Equating each one of the components of eqs. (106) and (109) we obtain the following integral equations for the determination of the transformed coordinates:

$$\frac{\int_{-1}^{\mu} \rho_2(\lambda, \mu, \varphi)(\lambda^2 - \mu^2) d\mu}{\int_{-1}^1 \rho_2(\lambda, \mu, \varphi)(\lambda^2 - \mu^2) d\mu} \\ = \frac{\int_{-1}^{\mu_T} \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T}{\int_{-1}^1 \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T} \quad (110) \\ \frac{\int_1^{\lambda} \rho_2(\lambda, \mu, \varphi)(\lambda^2 - \mu^2) d\lambda}{\int_1^\infty \rho_2(\lambda, \mu, \varphi)(\lambda^2 - \mu^2) d\lambda} \\ = \frac{\int_1^{\lambda_T} \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\lambda_T}{\int_1^\infty \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\lambda_T} \quad (111)$$

$$\frac{\int_0^{\varphi} \int_1^1 \rho_2(\lambda, \mu, \varphi)(\lambda^2 - \mu^2) d\mu d\lambda d\varphi}{\int_0^{2\pi} \int_1^1 \rho_2(\lambda, \mu, \varphi)(\lambda^2 - \mu^2) d\mu d\lambda d\varphi} \\ = \frac{\int_0^{\varphi_T} \int_1^1 \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T d\lambda_T d\varphi_T}{\int_0^{2\pi} \int_1^1 \rho_2(\lambda_T, \mu_T, \varphi_T)(\lambda_T^2 - \mu_T^2) d\mu_T d\lambda_T d\varphi_T} \quad (112)$$

Each one of these equations must then be solved by either a numerical procedure or by resorting to Padé approximants.

## DIRECT TREATMENT

We discuss here a simpler way to generate the integral equations for the local-scaling transformations of diatomic molecules. Applications of this method to polyatomic molecules (or solids) is discussed in Appendix B. Consider the diatomic molecule orthonormal orbital set:

$$\psi_i(\lambda, \mu, \varphi) = \phi_i(\lambda, \mu) e^{im_i\varphi} \quad (113)$$

and its associated one-particle density (which depends only on coordinates  $\lambda$  and  $\mu$ ):

$$\rho(\lambda, \mu) = \sum_{ij} C_{ij} \psi_i^*(\lambda, \mu, \varphi) \psi_j(\lambda, \mu, \varphi) \\ = \sum_{ij} \delta_{m_i m_j} \phi_i(\lambda, \mu) \phi_j(\lambda, \mu) \quad (114)$$

Let us assume that from the orthonormal set of one-particle functions  $\{\psi_i(\lambda, \mu, \varphi)\}$  we obtain the density-transformed orbitals:

$$\psi_i^T(\lambda, \mu, \varphi) = \sqrt{\frac{\rho_2(\lambda, \mu)}{\rho_1(\lambda_T, \mu_T)}} \psi_i(\lambda_T, \mu_T, \varphi_T) \quad (115)$$

We now impose the orthonormality condition on these transformed orbitals:

$$\left( \frac{R}{2} \right)^2 \int_1^\infty d\lambda \int_{-1}^1 d\mu \int_0^{2\pi} d\varphi (\lambda^2 - \mu^2) \\ \times \psi_i^{*T}(\lambda, \mu, \varphi) \psi_j^T(\lambda, \mu, \varphi) = \delta_{ij} \quad (116)$$

Substituting eq. (115) into eq. (116) we see that the orthonormality condition is now given by the differential equation:

$$d\lambda d\mu d\varphi (\lambda^2 - \mu^2) \rho_2(\lambda, \mu) \\ = d\lambda_T d\mu_T d\varphi_T (\lambda_T^2 - \mu_T^2) \rho_1(\lambda_T, \mu_T) \quad (117)$$

To integrate eq. (117), we assume the following functional form for the transformed coordinates:

$$\begin{aligned}\mu_T &\equiv \mu_T(\mu) \\ \lambda_T &\equiv \lambda_T(\lambda, \mu) \\ \varphi_T &= \varphi\end{aligned}\quad (118)$$

where we have explicitly set  $\varphi_T$  equal to  $\varphi$  in view of the fact that this coordinate fades out in the density of diatomic molecules. Using eq. (118), the differential relation, eq. (117), simplifies to:

$$\begin{aligned}d\mu d\lambda(\lambda^2 - \mu^2)\rho_2(\lambda, \mu) \\ = d\mu_T d\lambda_T(\lambda_T^2 - \mu_T^2)\rho_1(\lambda_T, \mu_T)\end{aligned}\quad (119)$$

Eq. (119) can be integrated over all space for both variables. This leads to an equality in the normalization of both densities. Another expression is obtained when  $\mu$  on the left-hand side is integrated from  $-1$  to  $\mu$  and  $\mu_T$  on the right-hand side from  $-1$  to  $\mu_T$  (while  $\lambda$  and  $\lambda_T$  are integrated over all space):

$$\begin{aligned}\int_{-1}^{\mu} d\mu \int_1^{\infty} d\lambda(\lambda^2 - \mu^2)\rho_2(\lambda, \mu) \\ = \int_{-1}^{\mu_T} d\mu_T \int_1^{\infty} d\lambda_T(\lambda_T^2 - \mu_T^2)\rho_2(\lambda_T, \mu_T)\end{aligned}\quad (120)$$

Also, from eq. (119) we can integrate  $\lambda$  on the left-hand side from  $1$  to  $\lambda$  and  $\lambda_T$  on the right-hand side from  $1$  to  $\lambda_T$  and then solve for  $d\mu_T/d\mu$ . However, another expression for  $d\mu_T/d\mu$  can be obtained when we integrate  $\lambda$  and  $\lambda_T$  from  $1$  to  $\infty$ . By equating the expressions for  $d\mu_T/d\mu$ , we obtain:

$$\begin{aligned}\frac{\int_1^{\lambda} d\lambda(\lambda^2 - \mu^2)\rho_2(\lambda, \mu)}{\int_1^{\infty} d\lambda(\lambda^2 - \mu^2)\rho_2(\lambda, \mu)} \\ = \frac{\int_1^{\lambda_T} d\lambda_T(\lambda_T^2 - \mu_T^2)\rho_2(\lambda_T, \mu_T)}{\int_1^{\infty} d\lambda_T(\lambda_T^2 - \mu_T^2)\rho_2(\lambda_T, \mu_T)}\end{aligned}\quad (121)$$

Eqs. (120) and (121) constitute the basis for the calculation of density transformations in diatomic molecules. Clearly, the transformed coordinate  $\mu_T(\mu)$  calculated by solving eq. (120) enters as a fixed quantity in eq. (121), which in turn allows us to determine  $\lambda_T(\lambda, \mu)$ . The alternative choice:

$$\begin{aligned}\lambda_T &\equiv \lambda_T(\lambda) \\ \mu_T &\equiv \mu_T(\lambda, \mu) \\ \varphi_T &= \varphi\end{aligned}\quad (122)$$

could not be used as it was observed to lead to numerical instabilities.

## Applications of Density Transformations to Diatomic Molecules

In this section we deal with applications of the density transformations discussed in eqs. (120) and (121) to some selected diatomic molecules. We discuss the nonvariational improvement brought about on the total energy when these transformations are applied to simple wave functions. In addition, we present results for the density-constrained kinetic energy minimization at fixed Hartree–Fock density (this procedure is equivalent to the Kohn–Sham *x-only* method).

Let us first consider the effect on the energy of applying these density transformations so as to achieve a nonvariational improvement of simple wave functions (constructed from limited basis sets). The transformations carry the initial density of these trial wave functions to the Hartree–Fock density. By means of this transformation a new orbital set and its corresponding 1-matrix [eq. (20)] can be constructed. By introducing this transformed 1-matrix into eqs. (18) and (19) the energy can then be evaluated through eq. (17). We employ, in the present calculations, the numerical diatomic molecule programs developed by Laaksonen, Pyykko, and Sundholm<sup>88</sup> and modified by Kobus et al.<sup>89</sup> These are numerical programs that apply the finite difference method to the solution of the diatomic molecule Hartree–Fock problem. These programs have been adapted by us for the purpose of including the density-transformation routines.

In Table VI, we present some results for  $\text{LiH}(^1\Sigma^+)$  and  $\text{Li}_2(^1\Sigma_g^+)$ , where the trial wave functions are the best-limited LCAO-MO (BL) of Ransil.<sup>90</sup> Each molecular orbital is constructed as a linear combination of atomic functions. The latter are optimized single- $\zeta$  Slater functions. As it can be seen from this table, for  $\text{LiH}(^1\Sigma^+)$ , the total energy of the BL wave function differs by 0.0175 hartree from the Hartree–Fock value. This distance is diminished considerably as a result of the density transformation, which lowers it to 0.0060 hartree. Perhaps the most interesting result in this respect is the improvement on the exchange energy that differs from the Hartree–Fock one in just 0.0001 hartree as opposed to 0.0248 hartree in the

**TABLE VI.**  
**Total, Exchange, and Kinetic Energies (in Hartrees) for Best Limited LCAO-MO (BL) and Their**  
**Density-Transformed MO for Diatomic Molecules LiH( $^1\Sigma^+$ ) and Li $_2$ ( $^1\Sigma_g^+$ ) (Hartree–Fock Results Included).**

Species	$R$	Method	$-E_{Total}$	$T$	$-E_x$	$-\epsilon_{HOMO}$
LiH( $^1\Sigma^+$ )	3.015	BL	7.9699	7.9788	2.1716	0.299
		LS-DFT	7.9814	7.9971	2.1467	0.300
		HF	7.9874	7.9913	2.1468	0.302
Li $_2$ ( $^1\Sigma_g^+$ )	5.051	BL	14.8415	14.8667	3.6125	0.181
		LS-DFT	14.8638	14.8961	3.5642	0.180
		HF	14.8716	14.8894	3.5653	0.182

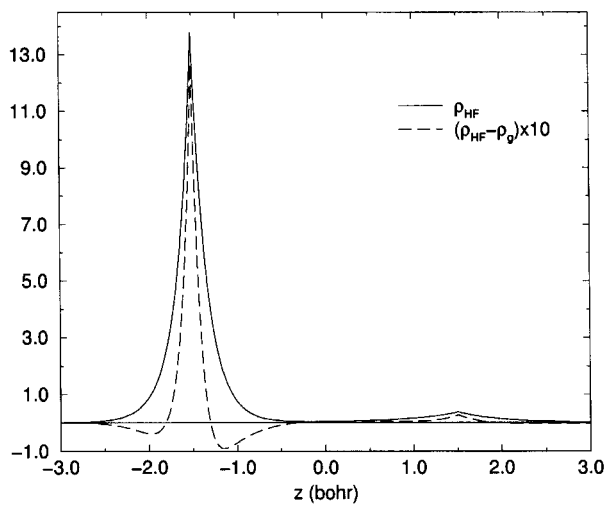
case of the untransformed wave function. Similar results are also obtained for the homonuclear diatomic molecule Li $_2$ ( $^1\Sigma_g^+$ ).

For completeness, we show in Figures 5 and 6 the difference between the HF and the BL densities (which in this case play the role in  $\rho_g$ ) for LiH( $^1\Sigma^+$ ) and Li $_2$ ( $^1\Sigma_g^+$ ), respectively. In these figures, this difference has been magnified by a factor of ten. These graphs illustrate how very slight redistributions in total density (such as those observed here) can lead to energy changes of the order of 0.01 hartree.

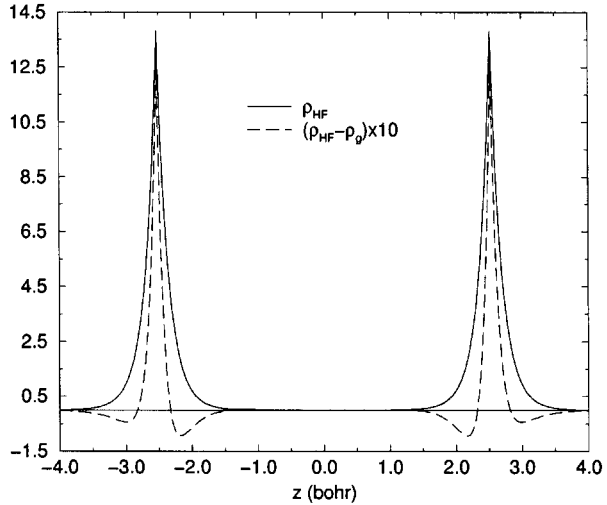
Variational calculation for diatomic molecules involving density transformations will be presented elsewhere.<sup>91</sup> It is clear that the energy functional described by eq. (17) can be minimized by introducing some parametric expression for the one-particle density,  $\rho$ . The results presented here for  $\rho = \rho_{HF}$  are, therefore, just upper bounds to this minimum.

As is well known, a density-constrained minimization of the kinetic energy of a noninteracting  $N$ -particle system is equivalent to solving the variational problem involved in the Kohn–Sham method. When this minimization is carried out with  $\rho = \rho_{HF}$  we have the exchange-only Kohn–Sham results.

For the kinetic energy minimization at the exchange-only level, we used two types of Hartree–Fock densities (when available): numerical densities obtained by the numerical HF program<sup>88,89</sup> and the analytical densities of Cade and Huo.<sup>92</sup> In Table VII we present results for the kinetic energy,  $T_s$ , the total and exchange energies, as well as for the highest occupies molecular orbital eigenvalue for the diatomic hydrides LiH( $^1\Sigma^+$ ), BeH( $^2\Sigma^+$ ), BH( $^1\Sigma^+$ ), and HF( $^1\Sigma^+$ ). For comparison, we included the corresponding Hartree–Fock values.



**FIGURE 5.** Hartree–Fock density and differences between HF and  $\rho_g$  densities for the molecule LiH( $^1\Sigma^+$ );  $R_e = 3.015$  bohr.



**FIGURE 6.** Hartree–Fock density and difference between HF and  $\rho_g$  densities for the molecule Li $_2$ ( $^1\Sigma_g^+$ );  $R_e = 5.051$  bohr.

**TABLE VII.**  
**Kohn–Sham  $x$ -Only Energy Values and Their Differences from Hartree–Fock Values for Selected Diatomic Hydrides (in Hartrees).**

Species/ $\Delta$	Method	$T_s$	$-E_{Total}$	$-E_x$	$\epsilon_{HOMO}$
LiH( $^1\Sigma^+$ ) $R = 3.015$ $\Delta$	HF	7.9913	7.9874	2.1468	0.302
	KS	7.9910	7.9870	2.1461	0.302
		0.0003	0.0004	0.0007	
	HF <sup>a</sup>	7.9913	7.9873	2.1468	0.302
	KS <sup>b</sup>	7.9909	7.9869	2.1460	0.302
$\Delta$		0.0004	0.0004	0.0008	
BeH( $^2\Sigma^+$ ) $R = 2.538$ $\Delta$	HF <sup>a</sup>	15.1494	15.1531	3.0859	0.313
	KS <sup>b</sup>	15.1478	15.1510	3.0822	0.309
		0.0016	0.0021	0.0037	
BH( $^1\Sigma^+$ ) $R = 2.329$ $\Delta$	HF	25.1200	25.1316	4.1325	0.348
	KS	25.1185	25.1300	4.1294	0.347
		0.0015	0.0016	0.0031	
HF( $^1\Sigma^+$ ) $R = 1.7328$ $\Delta$	HF	100.0267	100.0708	10.4283	0.650
	KS	100.0249	100.0686	10.4243	0.650
		0.0018	0.0022	0.0040	
	HF <sup>a</sup>	100.0274	100.0703	10.4287	0.650
	KS <sup>b</sup>	100.0253	100.0684	10.4246	0.650
		0.0021	0.0019	0.0041	

<sup>a</sup> Hartree–Fock–Roothan method. <sup>b</sup> KS method at fixed Hartree–Fock density.

The same type of analysis has been extended to the homonuclear diatomic molecules Li<sub>2</sub>( $^1\Sigma_g^+$ ) and F<sub>2</sub>( $^2\Sigma_g^+$ ), and also to the heteronuclear diatomic molecule LiF( $^1\Sigma^+$ ). The results are presented in Table VIII [for F<sub>2</sub>( $^2\Sigma_g^+$ ), the analytic Hartree–Fock densities were not available at the selected  $R$ ].

Because the calculation of  $T_s$  in the Kohn–Sham method is done by resorting to a minimum principle, these  $T_s$  values should lie below those of the Hartree–Fock kinetic energy. Similarly, the total Kohn–Sham exchange-only energies should be upper bounds to the Hartree–Fock ones. These variational constraints are satisfied by the results listed in Tables VII and VIII. Moreover, the exchange energies computed from the Kohn–Sham  $x$ -only orbitals are in close agreement with the Hartree–Fock values (and also lie above them). We also observe a striking similarity between the  $\epsilon_{HOMO}$  values [except for BeH( $^2\Sigma^+$ ), in all other cases the differences are of the order of, or less than, 1 millihartree].

To establish a common platform for valid comparisons with results of the Amsterdam group,<sup>93–96</sup> work is currently under way<sup>91</sup> with Hartree–Fock and “exact” densities provided to us by Gritsenko. Hopefully, this will allow us to assess the accuracy

of both approaches to the calculation of “exact” density functional quantities such as  $T_s$ ,  $T_c$ , the Kohn–Sham exchange, and correlation potentials, etc., for diatomic molecules.

## Extension to Polyatomic Systems

We comment here on two alternatives having to do with the application of local-scaling transformations to polyatomic systems. The first refers to a decomposition of a molecular system into atom-centered subsystems,<sup>50</sup> and the second to the treatment of subsystems in a periodic solid.

Let us rewrite the energy functional given by eq. (16) as:

$$E[\Phi_\rho] = \int d^3\vec{r}_1 \epsilon([\rho], \vec{r}_1) \quad (123)$$

where we assume that, in general, the energy density  $\epsilon([\rho], \vec{r}_1)$  is a multicenter function. Following Becke,<sup>97</sup> we assume that the multicenter integration can be carried out by decomposing the whole space into a collection of “fuzzy cells.” Under this decomposition, the energy functional

**TABLE VIII.**

**Kohn–Sham *x-only* Energy Values and Their Differences from Hartree–Fock Values for Selected Diatomic Homo- and Heteronuclear Molecules (in Hartrees).**

Species/ $\Delta$	Method	$T_s$	$-E_{Total}$	$-E_x$	$-\epsilon_{HOMO}$
$\text{Li}_2(^1\Sigma_g^+)$ $R = 5.051$ $\Delta$	HF	14.8894	14.8716	3.5653	0.182
	KS	14.8888	14.8708	3.5639	0.182
		0.0006	0.0008	0.0014	
	HF <sup>a</sup>	14.8905	14.8715	3.5659	0.182
	KS <sup>b</sup>	14.8898	14.8708	3.5645	0.181
$\Delta$		0.0007	0.0007	0.0014	
$\text{F}_2(^1\Sigma_g^+)$ $R = 2.0668$ $\Delta$	HF	198.5806	198.7729	19.9560	0.667
	KS	198.5738	198.7642	19.9405	0.665
		0.0068	0.0087	0.0155	
$\text{LiF}(^1\Sigma^+)$ $R = 2.955$ $\Delta$	HF	106.9840	106.9934	12.0021	0.476
	KS	106.9827	106.9906	11.9980	0.476
		0.0013	0.0028	0.0041	
	HF <sup>a</sup>	107.0065	106.9904	12.0166	0.468
	KS <sup>b</sup>	107.0038	106.9891	12.0127	0.469
		0.0027	0.0013	0.0039	

<sup>a</sup> Hartree–Fock–Roothan method.<sup>92</sup> <sup>b</sup> KS method at fixed Hartree–Fock density.

becomes:

$$E^{(n)}[\Phi_\rho] = \int d^3\vec{r}_1 \omega_n(\vec{r}) \epsilon([\rho^{(n)}], \vec{r}_1^{(n)}) \quad (124)$$

where  $\omega_n(\vec{r})$  is a relative weight function associated with a center,  $n$ ,<sup>97</sup> that is unity about nucleus  $n$ , but vanishes in a continuous and well-behaved manner near any other nucleus. It also satisfies the condition  $\sum_{n=1} \omega_n(\vec{r}) = 1$ . In terms of this decomposition,  $\epsilon([\rho^{(n)}], \vec{r}_1^{(n)})$  becomes an atom-centered functional generated by the spherically averaged local-scaling transformation carrying the vector  $\vec{r}^{(n)} \equiv (r^{(n)}, \theta^{(n)}, \varphi^{(n)})$  into  $\vec{f}^{(n)} \equiv (f^{(n)}, \theta^{(n)}, \varphi^{(n)})$ . Expanding the transformed molecular orbitals (about each nucleus  $n$ ) by:

$$\begin{aligned} \phi_{\rho,i}((r^{(n)}, \theta^{(n)}, \varphi^{(n)})) \\ = \sum_p C_{i(p)} \phi_{\rho,i(p)}((r^{(n)}, \theta^{(n)}, \varphi^{(n)})) \end{aligned} \quad (125)$$

and assuming the following separation in radial and angular coordinates:

$$\begin{aligned} \phi_{\rho,i(p)}((r^{(n)}, \theta^{(n)}, \varphi^{(n)})) \\ = R_{\rho, n, i(p)}(r^{(n)}) Y_{l_{i(p)}, m_{l_{i(p)}}}(\theta^{(n)}, \varphi^{(n)}) \end{aligned} \quad (126)$$

where for each component the following transformation applies:

$$R_{\rho, n, i(p)}(r^{(n)}) = \sqrt{\frac{\rho(r^{(n)})}{\rho_g(f^{(n)})}} R_{g, n, i(p)}(f^{(n)}) \quad (127)$$

we are led to atom-centered kinetic and exchange energy functionals of the type:

$$\begin{aligned} T^{(n)}[\Phi_\rho] = T_W^{(n)}[\Phi_\rho] + \int_0^\infty dr r^2 \omega_n(r) \rho^{5/3}(r) \\ \times \left[ (1 + \vec{r} \cdot \nabla \ln \lambda(r))^{4/3} \tau_N^{(n)} \right. \\ \left. + (1 + \vec{r} \cdot \nabla \ln \lambda(r))^{-2/3} \kappa_N^{(n)} \right] \end{aligned} \quad (128)$$

and:

$$\begin{aligned} E_x^{(n)}[\Phi_\rho] = -\frac{1}{2} \int_0^\infty dr_1 r_1^2 \sum_{k=0}^{k_{max}} \rho(r_1)^{(4+k)/3} \\ \times \left( \frac{1}{1 + \vec{r}_1 \cdot \nabla \ln \lambda(r_1)} \right)^{(k+1)/3} \chi_N^{(n)k}(f_1) \end{aligned} \quad (129)$$

Explicit expressions for the kinetic-energy and exchange-energy modulating factors,  $\tau_N^{(n)}$ ,  $\kappa_N^{(n)}$ , and  $\chi_N^{(n)}$ , have been given elsewhere.<sup>50</sup>



The second alternative, applicable mainly to periodic solids, takes advantage of the fact that, for these systems, the main drawback in applying DFT stems from the lack of an adequate description of the kinetic energy functional. We assume, in this case, the following expression for the kinetic energy functional:

$$T[\Phi_\rho] = \frac{1}{2} \sum_{i=1}^N \int dx \int dy \int dz \times \nabla_{\vec{r}} \phi_i^{*T}(x, y, z) \nabla_{\vec{r}} \phi_i^T(x, y, z) \quad (130)$$

where the density-transformed orbitals are given by eq. (B3) (see Appendix B).

Because most of the methods applied to solids rely on numerical integration, there is no need to generate explicit functionals, although the minimization of the energy is carried out by varying the density  $\rho(x, y, z)$ . Moreover, by taking the functional derivative of  $T[\Phi_\rho]$  with respect to the variable  $\rho$  the attractive possibility arises of doing direct molecular dynamics with respect to  $\rho$  and, hence, of bypassing the solution of the Kohn–Sham equations for these systems.

## Conclusions

In the present work, we have addressed, within the context the local-scaling transformation version of density functional theory, the generation of explicit functionals for first- and second-row atoms, as well as the application of density transformations to diatomic molecules.

In the work devoted to atoms, special emphasis has been placed on the problem of how to incorporate angular momentum and spin symmetry in the generation of these explicit functionals. The fact that a number of alternative methods<sup>68–77</sup> have been advanced in the context of conventional DFT is quite indicative as to a lack of general agreement in this area. A possible solution to this problem within the LS-DFT context has been presented here. Of particular interest in this respect are the explicit exchange functionals we have advanced in the third section for the multiplets of the carbon atom.

It is true enough, however, that one of the alluring aspects of conventional DFT is the universality of the functionals employed.<sup>98–100</sup> Nevertheless, there seems to be a limit (in terms of accuracy) as to what one can achieve with these universal functionals. In fact, there is a tendency to

restrain this universality to classes of systems and to search for particular functionals that meet the characteristics of given systems. On the other hand, the functionals that emerge from LS-DFT are not entirely universal in the sense that these functionals contain modulating factors that are system-specific. But, as has been shown in the case of atoms, these functionals do contain several of the elements appearing in the conventional universal functionals. For instance, in the kinetic energy functional given by eq. (23), in addition to the Weizsäcker term, there arises a Thomas–Fermi-like term that contains the usual factor  $\rho^{5/3}$ .

The analysis provided (in the subsection “Modulating Factors in Generalized Slater-Type Orbital Basis”) for the behavior of the kinetic-energy-modulating factor  $\tau$  for the aluminum atom shows the importance of this factor in giving rise to the shell structure of this atom. The connection (easily viewed in Fig. 1) between this factor and the charge distribution points toward the possibility of modeling this factor as a function of the one-particle density. For this reason, we consider the present results obtained in the context of LS-DFT as a guide toward attaining simpler and more universal functionals of  $\rho$ . It is quite likely that a complete universality is not possible, but at least we hope to develop simpler forms for the modulating factors that depend on both  $\rho$  and the atomic number  $Z$ .

In addition, the exchange-energy functional generated for atoms in the context of LS-DFT incorporates, in a natural fashion, the angular momentum characteristics of multiplet structure. Thus, the universal factors appear as a set  $\rho^{(4+k)/3}$ , where  $k$  is a variable that runs over values determined by the triangular angular momentum condition.<sup>60</sup> This result adds richness to density functional theory and opens the way to a more adequate treatment of multiplet structure as well as near-degeneracy. It is quite possible, in addition, to use these functionals as starting points for density-based modeling of the exchange-modulating factors.

There are three basic aspects of correlation energy that we have summarily addressed in the present article. The first is that, due to the emergence of the reference wave function,  $\Psi^R$ , the correlation energy can be decomposed into “long-range” and “short-range” contributions. The second is that the dynamical component of the long-range part (which is by far the dominant term) can be treated within the usual LS-DFT scheme and, hence, that explicit functionals can be readily ob-

tained by slightly modifying the methods already employed for  $\mathcal{E}[\rho, \Psi^{HF}]$ . The third is that the dynamical short-range correlation component can be treated by means of a cluster-type expansion expressed as an explicit functional of the one-particle density.

Elsewhere<sup>83</sup> we have shown how the leading term in a cluster expansion based on a single Slater determinant when transformed into an explicit energy density functional yields the universal factors  $\rho^{5/3}$ ,  $\rho^{4/3}$ , and  $\rho^{2/3}$ . This fact shows that there is considerable linkage between the correlation component of the energy with both the kinetic and exchange components. One would also expect similar results for cluster expansions based on a limited linear combination of Slater determinants.

The relevance of developing density transformations for diatomic molecules lies in that it is quite important to have exact results again which to assess the validity of approximations. In this respect, density transformations allow us to calculate accurate Kohn–Sham orbitals and potentials through a density-constrained kinetic energy minimization. For this reason, they represent a valid alternative to the usual DFT treatments.<sup>93–96</sup>

However, with respect to the generation of explicit density functionals for diatomic molecules, the situation is not as straightforward as it is for atoms. The reason is that the density transformations for prolate–spheroidal coordinates turn out to be rather complicated and hence the steps for going from these transformations to explicit density functionals are not evident. Nevertheless, exact results can be obtained in a numerical fashion. Moreover, these numerical results can be used to calibrate center-based functionals (or functionals for nonspherical atoms). This would correspond to a strategy whereby the functional for the whole molecule is decomposed into a collection of atom-centered functionals. This alternative has been discussed in ref. 50.

## Appendix A: Padé Approximants to One-Dimensional Isotropic Local-Scaling Transformations

The local-scaling transformation function,  $f(r)$ , can be explicitly written as a function of the one-particle density,  $\rho(r)$ , by using Padé approximants.<sup>51,101</sup> For a [1,1] Padé approximant, this

function becomes:

$$f(r) = r + \frac{2\rho_g(r)r\Delta N(r)}{2\rho_g^2(r)r^3 + \{\rho'_g(r)r + 2\rho_g(r)\}\Delta N(r)} \quad (\text{A1})$$

where:

$$\Delta N(r) = \int_0^r \rho(t)t^2 dt - \int_0^r \rho_g(t)t^2 dt \quad (\text{A2})$$

Expressions for  $f(r)$  involving other types of more complex Padé approximants have been presented elsewhere.<sup>51</sup>

## Appendix B: Nonisotropic Density Transformations for Cartesian Coordinates

In addition to the isotropic density transformations (or isotropic local-scaling transformations), which are characterized by eq. (1), we may consider also nonisotropic density transformations. In this case, we label the transformed vector as follows:

$$\vec{r}^T = (x^T, y^T, z^T) \quad (\text{B1})$$

where the transformed coordinates are not isotropic. For example, in the present case, we assume the following functional form for the transformed coordinates:

$$x^T = x^T(x), \quad y^T = y^T(x, y), \quad z^T = z^T(x, y, z) \quad (\text{B2})$$

Let us consider an orthonormal set  $\{\phi_i(x, y, z)\}$  from which, according to eq. (7), we obtain the transformed orbitals:

$$\phi_i^T(x, y, z) = \sqrt{\frac{\rho(x, y, z)}{\rho_g(x^T, y^T, z^T)}} \phi_i(x^T, y^T, z^T) \quad (\text{B3})$$

The orthogonality condition for the transformed orbitals is:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy dz \phi_i^{*T}(x, y, z) \phi_j^T(x, y, z) = \delta_{ij} \quad (\text{B4})$$

Substituting eq. (B3) in eq. (B4) we obtain:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy dz \frac{\rho(x, y, z)}{\rho_g(x^T, y^T, z^T)} \times \phi_i^*(x^T, y^T, z^T) \phi_i(x^T, y^T, z^T) = \delta_{ij} \quad (\text{B5})$$

Because, by assumption,  $\{\phi_i(x, y, z)\}$  is orthonormal, the orthonormality of the transformed set is guaranteed provided that:

$$dx dy dz \frac{\rho(x, y, z)}{\rho_g(x^T, y^T, z^T)} = dx^T dy^T dz^T \quad (\text{B6})$$

or, equivalently:

$$dx dy dz \rho(x, y, z) = \rho_g(x^T, y^T, z^T) dx^T dy^T dz^T \quad (\text{B7})$$

In view of eq. (B3), the differential relations embodied by eq. (B7) can be transformed into the corresponding integral equation for  $x^T(x)$  through the following integration:

$$\begin{aligned} \int_{-\infty}^x dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \rho(x, y, z) \\ = \int_{-\infty}^{x^T(x)} dx^T \int_{-\infty}^{\infty} dy^T \int_{-\infty}^{\infty} dz^T \rho_g(x^T, y^T, z^T) \end{aligned} \quad (\text{B8})$$

or:

$$\int_{-\infty}^{\infty} dx a(x) = \int_{-\infty}^{x^T(x)} dx^T a_g(x^T(x)) \quad (\text{B9})$$

or:

$$A(x) = A_g(x^T(x)) \quad (\text{B10})$$

Eq. (B10) is a transcendental equation that yields for  $x = x_i$  the transformed coordinate  $x_i^T = x^T(x_i)$ .

From eq. (B7), we have:

$$\begin{aligned} \frac{dx^T(x)}{dx} &= \frac{\int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \rho(x, y, z)}{\int_{-\infty}^{\infty} dy^T \int_{-\infty}^{\infty} dz^T \rho_g(x^T, y^T, z^T)} \\ &= \frac{a(x)}{a_g(x^T(x))} \end{aligned} \quad (\text{B11})$$

Similarly, from eq. (B7) we also get:

$$\begin{aligned} \frac{dx^T(x)}{dx} &= \frac{\int_{-\infty}^y dy \int_{-\infty}^{\infty} dz \rho(x, y, z)}{\int_{-\infty}^{y^T(x, y)} dy^T \int_{-\infty}^{\infty} dz^T \rho_g(x^T, y^T, z^T)} \\ &\equiv \frac{B(x, y)}{B_g(x^T(x), y^T(x, y))} \end{aligned} \quad (\text{B12})$$

Equating (B11) and (B12), we obtain:

$$B(x, y) = \frac{a(x)}{a_g(x)} B_g(x^T(x), y^T(x, y)) \quad (\text{B13})$$

Eq. (B13) is a transcendental equation, which, for  $x = x_i$  and  $y = y_j$ , yields the transformed coordinate,  $y^T(x_i, y_j) \equiv y_{ij}^T$ .

The transcendental equation for the function  $z^T(x, y, z)$  can also be obtained from eq. (B7) by writing:

$$\begin{aligned} \frac{dx^T(x)}{dx} \frac{\partial y^T(x, y)}{\partial y} &= \frac{\int_{-\infty}^{\infty} dz \rho(x, y, z)}{\int_{-\infty}^{\infty} dz^T \rho_g(x^T, y^T, z^T)} \\ &\equiv \frac{b(x, y)}{b_g(x^T(x), y^T(x, y))} \end{aligned} \quad (\text{B14})$$

and:

$$\begin{aligned} \frac{dx^T(x)}{dx} \frac{\partial y^T(x, y)}{\partial y} &= \frac{\int_{-\infty}^z dz \rho(x, y, z)}{\int_{-\infty}^{z^T(x, y, z)} dz^T \rho_g(x^T, y^T, z^T)} \\ &\equiv \frac{C(x, y, z)}{C_g(x^T(x), y^T(x, y), z^T(x, y, z))} \end{aligned} \quad (\text{B15})$$

Equating eqs. (B14) and (B15), we obtain the following transcendental equation:

$$\begin{aligned} C(x, y, z) &= \frac{b(x, y)}{b_g(x^T(x), y^T(x, y))} \\ &\times C_g(x^T(x), y^T(x, y), z^T(x, y, z)) \end{aligned} \quad (\text{B16})$$

For a fixed values of the coordinates,  $x = x_i$ ,  $y = y_j$ , and  $z = z_k$ , and using the transformed coordinates,  $x_i^T, y_{ij}^T$ , we can obtain, through eq. (B16),  $z^T(x_i, y_j, z_k) = z_{ijk}^T$ .

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